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DRY PAINT TRANSFER PROCESS AND PRODUCT

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FIELD OF THE INVENTION

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This invention relates generally to dry paint transfer techniques, and more particularly to the use of these techniques to produce exterior plastic car body members or panels with a paint coat applied in a separate production operation which can eliminate or greatly reduce the painting steps carried out in the manufacturing operations of a conventional automobile production plant.

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BACKGROUND

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Automotive design and manufacture present a unique set of problems in the selection of materials and processes used in the manufacture of automobile bodies. As a form of transportation, automobiles are unique because most buyers want a vehicle to have a certain individual styling. A recent trend in the automobile industry is toward production of distinctive vehicles

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1        styled to attract specific groups of consumers. This  
change has required the car builder to shift production  
from a few models manufactured in large volumes to a  
larger number of more distinctive body styles. These  
5        developments have demanded from the manufacturer both  
styling flexibility and reasonable tooling costs for  
each body style.

10      For many years, car body members and panels have  
been made predominantly from sheet metal. However, car  
builders now generally recognize that future use of  
plastics for exterior car body members and panels,  
rather than sheet metal, may provide a solution to  
meeting the demand for more unique body styling and  
reduced tooling costs. With the increasing concern for  
15     weight-reduction, car builders have also turned their  
attention to the use of plastics as an alternative to  
heavier metal parts. For instance, certain exterior car  
body parts of many automobiles now on the road are made  
from lighter-weight plastic. These parts include  
20     bumpers, rocker panels, fender extensions, window and  
door moldings, and the like.

25      As reported in Plastics World, November, 1986, p.  
30     et seq., a number of advanced corporate development  
programs now in process are also seeking solutions to  
the problem of commercially manufacturing from plastics  
the larger exterior car body panels such as hoods,  
roofs, deck lids, and in fact, the entire car body, if  
possible. The concept of making a production car body  
from a material other than sheet metal dates back to at  
30     least as early as the mid-1950's, when the Chevrolet  
Corvette was first manufactured with a fiberglass body.  
Developments in plastic resin technology in recent years  
have resulted in more sophisticated plastic materials of  
higher impact strength than fiberglass. Polycarbonates  
35     are an example. These developments in plastics

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1 technology have caused many plastics manufacturers, for  
about the last decade or so, to seek solutions to the  
problem of commercially producing the entire car body at  
a reasonable cost from these later-developed high-  
5 strength plastic materials. Recent development efforts  
have also been directed toward producing plastic car  
bodies from various alternative plastics molding  
processes, including use of SMC (sheet molding  
compounds) and RIM (reaction injection molding)  
10 techniques.

Development of a production process for making exterior car body members and panels from plastics requires solutions to a number of technical problems. These parts must be manufactured at reasonable costs for tooling, assembly and materials. The end product also must meet certain quality requirements. For instance, the resulting car body panel must have structural capabilities such as impact strength and resistance to mechanical stress necessary to compete with sheet metal.  
15 It must also have a paint coat with a defect-free and durable exterior surface. An automotive quality paint coat must meet certain specifications for a large number of physical properties in order to be capable of use as an exterior automotive paint coat. These properties include gloss; distinctiveness-of-image; hardness; abrasion resistance; weatherability such as UV resistance; impact strength; thermal stability, namely, resistance to extreme high and low temperatures; gasoline and acid resistance; cleanability; adhesion to the underlying car body panel; resistance to water and humidity exposure; and hiding ability or opacity of the paint coat.  
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In the past, a conventional production process for applying an exterior paint coat to car bodies made of sheet metal has involved transporting the preformed auto  
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1       bodies to application lines in the plant where the car  
2       bodies are dipped in paint, followed by transporting  
3       them to a separate location for baking the paint coat  
4       and waiting until the hardened paint coat dries  
5       thoroughly. Most paint systems today are acrylic  
6       enamels which are cross-linked into a hard, glossy,  
7       durable paint coat during baking. Following painting,  
8       the car bodies are transported back to the production  
9       plant for further assembly operations. The painting of  
10      plastic car body members has typically involved manually  
11      spray painting the plastic parts in a separate painting  
12      facility, followed by drying, and then transporting the  
13      finished parts back to the assembly operation.  
14      Conventional painting of sheet metal car bodies and  
15      plastic parts is expensive and is a significant factory  
16      problem with respect to environmental protection,  
17      workers' safety, corrosion treatment, and waste  
18      disposal. It is estimated that about one third of the  
19      total capital investment in an automobile production  
20      facility today is involved in painting car body members  
21      and panels.

22       In recent years, metalized laminating techniques  
23       have been used for forming a reflective, weather-  
24       resistant metal surface on molded plastic automotive  
25       trim parts. These techniques have not yielded plastic  
26       trim parts with a paint-coated surface capable of  
27       exterior automotive use. Such plastic trim parts have  
28       experienced difficulties in maintaining reflectivity and  
29       avoiding surface defects under mechanical impact and  
30       environmental exposure.

31       New car body applications of molded plastic  
32       materials can develop if the manufacturer can find a way  
33       to commercially produce plastic car body panels with a  
34       paint coat having the durability and appearance  
35       properties necessary for exterior automotive use.

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1      Moreover, if in-mold painting or coating processes can  
be developed as an alternative to conventional auto  
painting, then auto assembly plants can be more compact,  
and capital costs and environmental and safety problems  
5      associated with conventional car painting at the factory  
site can be avoided.

Many corporate product development efforts have  
sought alternatives to conventional painting of molded  
plastic exterior car body panels and parts, but without  
10     any known success to date. A number of problems must be  
overcome to develop an economical production-type paint  
system and process for applying a paint coat capable of  
exterior automotive use for molded plastic exterior car  
body panels and parts so as to eliminate conventional  
15     spray painting operations. For instance, use of the  
cross-linked acrylic enamel paint systems which are  
commonly baked on the sheet metal car bodies to produce  
a tough, glossy finish cannot be used in painting  
plastic car bodies because of temperature limitations.  
20     One approach, which is the subject of this invention,  
involves developing a paint-coated laminate which can be  
used to replace the conventional painted finish on the  
exterior of an automobile body. The laminate is made  
from a paint coat applied to a casting sheet by paint  
25     coating techniques. The dried paint coat is then  
transferred from the casting sheet to a laminate panel  
by dry paint transfer techniques. The coating operation  
permits use of high temperature resistant paint systems  
capable of producing a tough, glossy finish. The  
30     laminate is later thermoformed into a complex three-  
dimensional shape and then bonded or integrally molded  
to an underlying plastic car body member or panel.  
Injection-cladding techniques can be used to manufacture  
a molded plastic part and simultaneously bond the  
35     laminate to the exterior of the molded plastic part.

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1        A number of technical problems must be overcome in  
order to use such a laminate in a thermoforming and  
injection-cladding process, while maintaining a defect-  
free painted surface with high gloss and durability  
5        properties throughout the thermoforming and injection-  
cladding steps. For instance, the laminate must be heat  
and vacuum-formable into a complex three-dimensional  
shape without cracking, deglossing, stress whitening or  
creating other surface defects. A paint coat on such a  
10      laminate can require a substantial amount of pigment in  
order to provide the necessary color density or opacity  
and distinctiveness-of-image. However, it has been  
found that use of pigments in a paint coat can cause  
deglossing of the surface when a paint-coated laminate  
15      is thermoformed. Deglossing may even occur in a  
nonpigmented clear coat during thermoforming.

In addition to surface gloss requirements, the  
finished paint coat must be defect-free. Defects must  
not be produced by the thermoforming step, and the  
20      laminate also must be bonded or molded to the underlying  
plastic substrate in a manner that hides any defects  
that may be present in the substrate material.

Moreover, a finished paint coat may have a  
reasonably high surface gloss, but still not have the  
25      desired visual appearance known as distinctiveness-of-  
image. This property relates to the mirror-like  
character of the finish and is measured by the clarity  
of an image reflected by the finished surface. It is  
difficult, in a thermoforming operation, to produce an  
30      exterior automotive paint coat with a high gloss level  
and a high distinctiveness-of-image.

Durability properties are also critical in  
producing a paint coat capable of exterior automotive  
use. The paint coat must avoid exhibiting defects when  
35      exposed to mechanical impact and avoid deterioration of

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1       the surface from exposure to chemicals and to the  
weather.

5       A paint system that produces the toughness or  
hardness necessary for exterior automotive use also must  
have the elongation properties and heat resistance  
necessary to allow thermoforming of the paint coat into  
complex three-dimensional shapes without cracking,  
deglossing, producing stress lines or other surface non-  
uniformities, or otherwise degrading the finish. Large  
10      pigment levels also adversely affect the strength and  
alter elongation properties of the paint coat. In  
addition, reliable bonding of the paint coat to the  
laminate and bonding of the laminate to the underlying  
substrate material are essential.

15      Thus, the desired paint system should have a  
critical combination of many physical properties in  
order to produce a surface capable of exterior  
automotive use, while retaining desired surface  
characteristics after the laminating, thermoforming and  
20      injection-cladding or molding steps have been carried  
out. However, some physical properties tend to be  
mutually incompatible in such a process. For instance,  
a paint system may have good qualities of durability  
such as hardness, toughness, weatherability and the  
25      like; but the same paint system may not have sufficient  
elongation to be heat-formed into a complex shape  
without cracking or otherwise losing its durability  
properties. Other paint systems may degloss when heat-  
formed into a complex shape. Some paint systems have  
30      sufficient elongation to permit thermoforming into the  
desired complex shape, but they are too soft and  
therefore lacking in the necessary hardness or  
durability properties.

35      In summary, there is a need for an economical  
production process for manufacturing highly contoured

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1       molded plastic exterior car body members or panels with  
a laminated paint coat having both the durability and  
the gloss and other appearance properties sufficient for  
exterior automotive use. Laminating techniques for  
5       applying a paint coat to such a molded plastic part can  
provide a valuable alternative to conventional painting  
of exterior car body members. Certain properties, such  
as glass-smooth, defect-free surfaces and uniform paint  
coats, are better produced by laminating techniques than  
10      by conventional painting. Capital costs also can be  
reduced and environmental problems can be alleviated.  
Laminating techniques require, in addition, however, a  
paint system and processing techniques capable of  
producing and maintaining, throughout processing, the  
15      durability and elongation properties, opacity, gloss and  
distinctiveness-of-image levels, and defect-free surface  
necessary for exterior automotive applications. The  
present invention solves these problems.

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1        SUMMARY OF THE INVENTION

Briefly, one embodiment of this invention provides a process for manufacturing a molded plastic article having a finished paint coat with surface properties meeting criteria for exterior automotive use. These include properties providing predetermined durability, gloss and other appearance characteristics in the finished paint coat. In this process, the paint coat is applied to a three-dimensionally shaped exterior surface of an intermediate laminate by a combination of paint coating, dry paint transfer-laminating, and thermoforming techniques. The thermoformed laminate then can be bonded to or molded to an underlying plastic substrate, for example, by injection-cladding techniques, with the paint coat maintaining properties sufficient for exterior automotive use throughout these processing steps. The invention is described herein in the context of a paint coat applied to the surface of a plastic car body member or panel, but the invention is also applicable to other articles of manufacture having a paint coat with properties similar to those required for exterior automotive use.

Considering the application of the invention to a process for making a plastic exterior car body panel, a paint coat comprising a synthetic resinous material is coated in thin-film form onto a flexible, heat-resistant temporary casting sheet. The paint coat is dried on the sheet sufficiently to harden it and transfer a predetermined exterior surface gloss level from the casting sheet to the paint coat. The paint coat may comprise a clear coat and a separate pigmented color coat. The clear coat and color coat may be formed as separate thin-film coatings which are dried and then bonded to one another. The color coat, in combination with the clear coat, provides a composite paint coat

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1 having the durability, gloss and other appearance  
properties necessary for exterior automotive use. The  
paint coat is transferred to a semirigid, thermoformable  
5 synthetic resinous backing sheet so that the paint coat  
provides the exterior surface of the paint-coated  
backing sheet. The laminate formed by the backing sheet  
and the bonded paint coat is thereafter thermoformed to  
produce a three-dimensionally shaped preformed laminate,  
while still retaining durability, gloss and other  
10 appearance properties necessary for exterior automotive  
applications. The thermoforming step can produce  
substantial elongation of the paint coat. The paint  
coat is capable of elongating from about 50% to about  
150%, or more, during thermoforming, without significant  
15 loss of its exterior automotive durability, gloss and  
other appearance properties. In a subsequent injection-  
cladding step, for example, a synthetic resinous  
substrate material is injection molded behind the  
preformed paint-coated laminate to bond the laminate to  
the substrate. This forms a molded plastic article with  
20 a painted surface which retains the exterior automotive  
surface characteristics. The substrate can be an  
exterior body panel of a motor vehicle. The substrate  
material normally may have a substandard surface finish,  
but the backing sheet absorbs surface defects in the  
25 substrate material during the injection-cladding step so  
as to retain the minimum surface defect level and gloss  
required of an exterior automotive paint coat.

In one embodiment, the paint coat comprises a  
30 fluorinated polymer and acrylic resin-containing paint  
system with thermoplastic properties. The relative  
amounts of the fluorinated polymer and acrylic resin  
components in the paint coat formulation provide a  
sufficient level of resistance to deglossing and  
35 sufficient elongation for the laminate to be

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1       thermoformed into complex three-dimensional shapes while  
          providing sufficient durability and appearance  
          properties for the finished product to be useful as an  
          exterior automotive body member or panel.

5       In one embodiment in which the paint coat comprises  
          an exterior clear coat and an underlying color coat  
          bonded to the clear coat, the clear coat can be formed  
          from a fluorinated polymer and acrylic resin-containing  
          coating. In this case, the clear coat can provide the  
10      majority of the durability, gloss and other appearance  
          properties necessary for use as an exterior automotive  
          paint coat. The color coat also can comprise a thermo-  
          plastic fluorinated polymer and acrylic resin-containing  
          paint system. Other paint systems compatible with the  
15      clear coat and the backing sheet also can be used.

20      In one form of the invention, the fluorinated  
          polymer component comprises polyvinylidene fluoride  
          (PVDF), and the acrylic resin component can be a  
          polymethyl methacrylate resin, a polyethyl methacrylate  
          resin, or mixtures thereof, including copolymers  
          thereof. One finished product having a surface capable  
          of exterior automotive use is made from a paint system  
          comprising from about 50% to about 70% PVDF and from  
          about 30% to about 50% acrylic resin, by weight of the  
25      total PVDF and acrylic solids, exclusive of the pigment.

30      This invention also provides an exterior automotive  
          quality paint coat having unusually high gloss and  
          distinctiveness-of-image (DOI) along with other  
          durability properties sufficient for exterior automotive  
          use. This embodiment of the invention includes a  
          thermoformable laminate having a paint coat bonded to it  
          in which the paint coat, prior to casting on a casting  
          sheet, was prepared as a solution of vinylidene fluoride  
          in acrylic resin. The paint coat comprises at least a  
35      clear coat of vinylidene fluoride and acrylic resin

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1       coated from solution, which produces thermoformed  
laminates with high combined gloss and DOI levels. Good  
combined gloss and DOI levels have been obtained  
experimentally when the clear coat and pigmented base  
5       coat both are prepared as a solution of vinylidene  
fluoride in the acrylic resin. In one experimental test  
of a finished car body panel, a 60° gloss level of  
greater than about 75 gloss units and a DOI approaching  
about 90 units were achieved.

10      Different forms of the invention are disclosed  
herein. One embodiment comprises a thermoformable  
laminate having a paint coat with properties capable of  
use in forming an exterior automotive finish on a  
plastic exterior car body panel. A further embodiment  
15      of the invention provides a process for applying a paint  
coat to an exterior body panel of a motor vehicle so  
that the paint coat in its finished form has the dura-  
bility, gloss and other appearance properties necessary  
for exterior automotive use. Another embodiment of the  
20      invention comprises a pressure-sensitive adhesive-backed  
paint-coated laminate capable of use in automotive paint  
coat repair.

25      Thus, the present invention provides a process and  
articles of manufacture in which a laminated exterior  
paint coat ultimately forms an exterior finish on a  
highly contoured surface of a molded plastic article.  
The paint coat has a sufficient combination of  
elongation and resistance to deglossing to withstand  
30      thermoforming without disrupting the high gloss surface  
originally present, while retaining the durability and  
appearance properties sufficient to be useful as an  
exterior paint coat for a plastic car body panel.

35      These and other aspects of the invention will be  
more fully understood by referring to the following  
detailed description and the accompanying drawings.

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1       DRAWINGS

5       FIG. 1 is a semi-schematic perspective view illustrating an automobile which may have one or more of its exterior body members or panels made from a molded plastic substrate having a paint coat produced according to principles of this invention.

10      FIG. 2 is a front elevation view illustrating a rear window panel section of a motor vehicle in which an exterior paint coat is formed on the surface of the window panel according to principles of this invention.

15      FIG. 3 is a cross-section taken on line 3-3 of FIG. 2 for illustrating the complex three-dimensional shape of the paint coat transferred to the exterior surface of the window panel.

20      FIG. 4 is a schematic cross-sectional view illustrating one embodiment of a paint-coated carrier sheet used in the dry paint transfer-laminating steps of this invention. Film thicknesses are exaggerated in size and not to scale, for simplicity.

25      FIG. 5 is a schematic side elevation view illustrating a paint coating step of the process.

30      FIG. 6 is a schematic side elevation view illustrating a laminating step of the process.

35      FIG. 7 is a schematic cross-sectional view illustrating a dry composite paint coat transferred to a backing sheet during the laminating step. Film thicknesses are exaggerated in size and not to scale, for simplicity.

40      FIG. 8 is a schematic view illustrating a thermoforming step of the process in which a paint-coated laminate is heated prior to vacuum forming.

45      FIG. 9 is a schematic view illustrating another thermoforming step in the process.

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1 FIG. 10 is a schematic cross-sectional view  
illustrating a preliminary step in an injection-cladding  
step of the process.

5 FIG. 11 is a schematic cross-sectional view  
illustrating a substrate material injection-molded  
behind the thermoformed laminate in an injection mold.

10 FIG. 12 is schematic cross-sectional view  
illustrating the composite cross-sectional structure of  
the finished molded plastic article having exterior  
paint coat. Film thicknesses are exaggerated in size  
and not to scale, for simplicity.

15 FIG. 13 is a graph illustrating a general  
relationship between surface gloss and the relative  
amounts of polyvinylidene fluoride and acrylic resin  
contained in one embodiment of the paint coat.

20 FIG. 14 is a schematic cross-sectional view  
illustrating one embodiment of a laminate having a dry  
paint film and a pressure-sensitive adhesive backing for  
use in automotive paint coat repair, according to  
principles of this invention.

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1        DETAILED DESCRIPTION

5        A paint coat with a surface capable of exterior automotive use is applied to a molded plastic article by a combination of paint coating, dry paint transfer-laminating, and thermoforming techniques for forming a paint-coated laminate which is then bonded to or molded to an underlying plastic substrate. The thermoformed laminate can be bonded to the substrate by injection-cladding techniques. The exterior automotive properties 10 of durability, gloss and other appearance criteria are produced and maintained throughout the process.

15       FIGS. 1 through 3 illustrate one embodiment of the dry paint transfer process and product in which an exterior automotive paint coat is transferred to an exterior body member or panel of an automobile 20. In the illustrated embodiment, the paint coat is transferred to the exterior surface of a rear window panel or molding 22 of the vehicle. The rear window molding can be injection-molded from a wood-filled synthetic 20 resinous plastic substrate 24 which forms the structural portion of the panel. The paint coat 26 can be transferred to the exterior surface of the substrate by the paint coating, dry paint transfer-laminating, thermoforming and injection-cladding techniques 25 described below. The paint coat 26 has properties useful in an exterior automotive paint coat, and these properties are also described in more detail below. Use of the process and article of this invention is described in the context of exterior car body members 30 and panels, although other end uses of the process and article also are possible, without departing from the scope of the invention. For simplicity, exterior car body members or panels are referred to herein as car body panels.

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1        The plastic substrate material 24 can contain large  
amounts of filler materials which can produce a normally  
substandard surface on the substrate. In carrying out  
the invention, the paint coat 26 is transferred to the  
5        surface of the substrate so that any imperfections in  
the underlying structural surface are absorbed by the  
laminate, thus presenting a perfectly smooth,  
unblemished paint coat having properties sufficient for  
exterior automotive uses. The rear window molding  
10      serves as an example of the type of highly contoured  
exterior surface to which the paint coat can be  
transferred. Referring to the rear window molding 22 in  
FIGS. 2 and 3, the molding has a large oblong-shaped  
window opening 28 with a wide border 30 having a highly  
15      contoured exterior surface extending around the window  
opening. The complexly shaped, multiple contour surface  
includes a curved outer ridge 32 of tapered cross-  
section extending around the periphery of the molding, a  
longitudinally curved and narrow recessed region 34  
20      extending inside the outer ridge, and a wide border  
section 36 of raised elevation inside the recessed  
region 34 extending around the entire periphery of the  
window opening. The wide border region 36 is at the  
same elevation as the surface of a wide end member 38 at  
25      one of the window opening. An inside edge 40 of the  
wide border section 36 has a tapered cross-sectional  
thickness and extends around the inside of the window  
opening. As represented in FIGS. 2 and 3, the exterior  
automotive paint coat 26 is adhered to the complexly  
30      shaped exterior surface of the rear window molding, but  
the paint coat also can provide a durable, high gloss  
exterior surface useful on other car body panels of  
various irregularly shaped three-dimensional surface  
configurations, as well as other articles of  
35      manufacture.

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1        Paint Coat

5        The process first includes the step of coating a paint coat, or a portion of a paint coat, onto one or more temporary carrier sheets. FIG. 4 illustrates one embodiment of a paint-coated carrier 41 which includes, in combination, a flexible, foldable, heat-resistant, self-supporting carrier sheet 42, also referred to in the art as a casting film; and a transferable, adherent, flexible paint coat 44 coated onto one surface of the carrier. The paint coat 44 is a non-self-supporting, 10      flexible synthetic resinous dry film-form coating. The paint coat 44 can comprise a combination exterior clear coat and a color coat, or a combination exterior clear coat and a tint coat; or the paint coat may comprise a single dry film-form coating of a pigmented synthetic 15      resinous material having the exterior automotive properties described below. In a presently preferred form, the paint coat 44 includes a clear coat 45 coated over the carrier and dried, and a color coat 46 on the dried clear coat. The color coat can be coated onto the dried clear coat. Alternatively, the clear coat and the color coat can be separately coated onto corresponding carrier sheets and dried on their respective carriers. The color coat then can be later bonded to the clear 20      coat. The combination clear coat and color coat are referred to herein as the paint coat 44, or a composite 25      paint coat, for simplicity.

30        The paint-coated carrier also optionally can include a size coat 47 coated on the dried color coat. The size coat provides adhesion to a backing sheet in a subsequent laminating step. In one embodiment, described below, a thermoplastic polyolefin backing sheet is used, and a thermoplastic chlorinated polyolefin size coat provides superior adhesion between 35      the paint coat and the backing sheet.

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1        The carrier sheet 42 is preferably a polyester  
casting film having a high gloss surface 48. The  
carrier can be a polyester film such as Mylar (a  
trademark of DuPont), American Hoechst 3000 polyester  
5        film, or the like. The preferred film thickness of the  
carrier sheet is about two mils. Polyester films are  
preferred because the high gloss surface 48 is capable  
of transferring a high gloss level to a surface 49 of  
the clear coat 45 in contact with the carrier, where the  
10      transferred gloss level is sufficient for exterior  
automotive use. Alternatively, the coatings can be cast  
on a polished metal belt. If the color coat is cast on  
a separate carrier sheet, the surface gloss imparted to  
the color coat from the carrier is not critical. The  
15      polyester carrier film has a sufficiently high heat  
resistance to resist axial elongation under the  
temperatures applied during subsequent paint coat drying  
and laminating steps. The clear coat may be applied to  
the polyester carrier film without a release coat on the  
20      high gloss surface 48 of the carrier. This can avoid a  
separate coating, which might detrimentally affect  
transfer of the high gloss surface from the carrier to  
the surface 49 of the clear coat. The formulation of  
the clear coat is such that the clear coat can be easily  
25      transferred from the carrier sheet and can replicate the  
high gloss surface of the carrier after the clear coat  
dries and after subsequent dry paint transfer-laminating  
steps in which the paint coat is transferred from the  
carrier to a laminate described below.

30      As an optional step, a thin film of wax (not shown)  
can be coated onto the carrier sheet and dried, followed  
by coating the clear coat 45 over the thin film of wax.  
The wax is coated in a film thickness (less than 0.01  
mil and preferably 0.001 mil) that avoids any adverse

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1       effect on the clear coat replicating the surface gloss  
of the carrier.

5       The clear coat 45 is a transparent or substantially transparent thermoplastic synthetic resinous coating composition coated in thin-film form onto the surface of the carrier sheet in a liquid state. Heat is later applied to the clear coat to dry it, without cross-linking the resin, while the clear coat is on the carrier. The preferred dry film thickness of the clear  
10      coat is about 0.5 to about 1.5 mils. Preferably, the clear coat is coated onto the carrier sheet by a reverse roll coating process illustrated in FIG. 5, although the clear coat can be applied by gravure printing, or other conventional coating techniques. Referring to the  
15      reverse roller coating process of FIG. 5, the clear coat lacquer 46 is contained in a coating pan 50 having a lacquer inlet 52 in the main portion of the pan and a lacquer drain 54 on an opposite side of a weir 56. An applicator roll 58 rotates to pick up the lacquer from  
20      the pan and coat it onto a previously uncoated polyester film 42 which passes over a guide roll 60 and then passes between the applicator roll and a rubber backup roll 62. A metering roll 64 adjacent the applicator roll rotates in the same direction as the applicator roll.  
25      A doctor blade 66 wipes the surface of the metering roll to properly control the thickness of the coating on the applicator roll. The adjustable gap between the metering roll and the applicator roll controls the thickness of the coating on the surface of the applicator roll. The coating picked up by the applicator roll is then coated onto the polyester film 42 as the film passes into contact with the reverse-rotating applicator roll. The applied coating on the film is shown at 68. The coated film then passes to a  
30      drying oven.  
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1        The clear coat is dried at oven temperatures in the  
range from about 250°F to about 400°F. Preferably, the  
clear coat is dried in multiple zones spaced apart along  
the long axis of the paint-coated carrier, in line with  
5        the reverse roll coater. A preferred drying technique  
involves use of three heating zones, with a  
progressively higher temperature applied in each  
successive zone. The solvent gases contained in the  
clear coat are essentially all driven off in the multi-  
10      stage drying process. The same multi-stage drying  
process is used for drying the color coat 46 and the  
size coat 47. The polyester carrier is resistant to  
heat at temperatures greater than about 450°F, so the  
carrier does not deform during the drying step. The  
polyester carrier film thickness of about two mils  
15      assists the film in resisting elongation during the  
drying steps. This ensures a high gloss level being  
replicated by the surface 49 of the dried clear coat  
from the high gloss surface 48 of the carrier. This  
also makes it possible to use high temperature-  
resistant, high gloss paint systems which cannot be  
20      applied to and dried on plastic substrates directly  
because of temperature limitations of the plastic  
materials.

25      The clear coat formulation produces a dry film-form  
exterior film which, in combination with the underlying  
color coat, produces a composite paint coat having  
properties useful as an exterior automotive paint coat.  
Such a paint coat is principally characterized by a  
30      combination of exterior automotive durability properties  
and gloss and other appearance properties of the  
finished paint coat. The specifications for a paint  
coat for exterior automotive use, as defined herein,  
include the mechanical properties of hardness; abrasion  
35      resistance; thermal stability, including heat

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1 resistance; resistance to gasoline and acids; cleanability; adhesion; certain weatherability properties such as UV resistance and resistance to water and humidity exposure; and impact strength. For  
5 simplicity, these properties are referred to collectively herein as "durability properties".

10 Weatherability, which is measured, in part, by UV resistance properties, is a durability property commonly used in the art to define standards for an exterior automotive paint coat. To measure UV resistance can require long-term exposure testing of the paint coat, for a period of two years in one test method. Certain  
15 long-term UV tests of the paint coat of this invention have not been completed to date, but other short-term accelerated UV resistance and weatherability tests of the paint coat have been completed and are described below.

20 In addition to durability properties, the specifications for an exterior automotive quality paint coat also include tests to measure the visual appearance qualities of the finished surface. These criteria include gloss, distinctiveness-of-image (DOI), dry film thickness and hiding ability or opacity of the paint coat. These properties are referred to collectively  
25 herein as "gloss and other appearance properties".

Thus, a paint coat can have a combination of pre-determined physical properties that collectively define whether the paint coat is capable of use as an exterior automotive paint finish. Generally, the paint coat of  
30 this invention, in dry film-form, provides a combination of the above-described durability and appearance properties, including gloss, which enables the paint coat to function as an exterior automotive paint coat.

35 The criteria used to define whether a paint coat is sufficient for exterior automotive use are not uniform

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1 throughout the automobile industry. Certain standards  
can vary from one auto manufacturer to the next, and  
from one car model to the next for a given auto manufac-  
turer. Most criteria used to define an exterior  
5 automotive quality surface for the process of this  
invention have been adopted from specifications and test  
methods used in certain General Motors Fiero and Pontiac  
Grand AM test programs. These criteria are disclosed  
herein as an example of techniques that can be used to  
10 measure whether a paint coat has sufficient properties  
for exterior automotive use, although other combinations  
of test criteria and test methods can also be used for  
this purpose. The specifications and test methods for  
measuring the properties of the exterior automotive  
15 paint coat of this invention are described in detail  
below.

In addition to the properties of durability and  
appearance, the clear coat formulation also imparts to  
20 the composite paint coat sufficient elongation at  
thermoforming temperatures to enable the paint coat to  
be thermoformed into complex three-dimensional shapes  
without deglossing of the clear coat and without  
reducing any durability property below that required for  
an exterior automotive surface. In one embodiment, the  
25 paint coat is thermoformed at temperatures from about  
280°F to about 450°F. A laminate having the clear coat  
as its exterior surface is capable of being thermoformed  
at these temperatures while maintaining the durability  
and appearance properties of the composite paint coat.  
30 Elongation of the paint coat can be substantial when  
forming the complex three-dimensional shapes of the  
finished article. Elongation of the clear coat (and the  
composite paint coat) can be greater than about 50%, and  
often greater than 100%, to form a highly contoured  
35 finished article. Plastic car body members and panels

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1 often require such deep draw forming. The clear coat  
also is capable of maintaining the durability and  
appearance properties of the paint coat during a  
subsequent injection molding step.

5 The clear coat is formulated from a transparent  
thermoplastic (non-cross-linked) synthetic resinous  
coating composition. The thermoplastic properties allow  
the clear coat, in dry film-form, to soften and deform  
and be vacuum-formable at thermoforming temperatures,  
10 while still retaining exterior automotive durability  
properties, gloss and other appearance properties after  
the heated and three-dimensionally shaped film-form  
coating returns to its stable or hardened condition. In  
dry film-form, the clear coat has an extensibility in  
15 the range from about 40% to about 150% or more, at a  
film thickness from about 0.5 to about 1.5 mils, and at  
thermoforming temperatures from about 280°F to about  
450°F.

20 In one embodiment, the clear coat comprises a blend  
of a thermoplastic fluorinated polymer and an acrylic  
resin. The clear coat preferably contains the fluori-  
nated polymer and acrylic resin as its principal  
components. The fluorinated polymer component is  
preferably a thermoplastic fluorocarbon such as  
25 polyvinylidene fluoride (PVDF). The fluorinated polymer  
also can include copolymers and terpolymers of  
vinylidene fluoride. One thermoplastic fluorocarbon  
useful in the clear coat is the polyvinylidene fluoride  
known as Kynar, a trademark of Pennwalt Corp. This  
30 polymer is a high molecular weight (400,000) polymer  
which provides a useful blend of durability and chemical  
resistance properties. Generally, a high molecular  
weight PVDF resin, with a weight average molecular  
weight of about 200,000 to about 600,000 is used.

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1        The acrylic resin component of the clear coat can  
be a polymethyl methacrylate, or a polyethyl  
methacrylate resin, or mixtures thereof, including  
methacrylate copolymer resins, and minor amounts of  
5        other comonomers. The clear coat also can include minor  
amounts of block copolymers and/or compatibilizers to  
stabilize the blended PVDF and acrylic resin system and  
provide compatibility between films.

10      In one embodiment, a principal component of the  
acrylic resin contained in the clear coat is a medium  
molecular weight polymethyl methacrylate resin such as  
Elvacite 2010, a trademark of DuPont. (In all further  
15      references to Elvacite resins herein, it should be noted  
that Elvacite is a trademark of DuPont for a group of  
its acrylic resins.) In another embodiment, a principal  
component of the acrylic resin for the clear coat can be  
a high molecular weight polyethyl methacrylate resin  
such as Elvacite 2042. The acrylic component of the  
clear coat also can comprise a mixture of Elvacite 2010  
20      and a medium-to-high molecular weight polymethyl meth-  
acrylate resin such as Elvacite 2021. In a further  
embodiment, the acrylic resin component can comprise  
Elvacite 2042 and a low molecular weight polyethyl  
methacrylate resin such as Elvacite 2043. Other similar  
25      combinations of acrylic resins, their homopolymers and  
copolymers, may be used as a component of the clear  
coat. Generally, the acrylic resin component has a  
relatively high weight average molecular weight of about  
50,000 to about 400,000.

30      The PVDF and acrylic-based clear coat formulation  
can be prepared as a solution of PVDF in the acrylic  
resin and solvent. Experimental tests of finished car  
body panels, in which the paint coat has been prepared  
35      from a solution of PVDF in acrylic resin, have  
demonstrated high levels of gloss and distinctiveness-

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1       of-image. The experimental test results are described  
in Example 11 below.

5       The PVDF and acrylic-based clear coat formulation  
also can be prepared as a dispersion of the PVDF in a  
solution of the acrylic resin. In one embodiment, the  
clear coat formulation can be prepared by mixing the  
acrylic resin with a suitable organic solvent and  
applying heat to dissolve the resin. The mixture is  
then allowed to cool sufficiently before adding the PVDF  
10      component so that the PVDF will not dissolve, but will  
be maintained as a dispersion in the acrylic-solvent  
based mixture. By maintaining the PVDF component as a  
dispersion in the clear coat, solvent evaporation during  
drying of the clear coat can be improved.

15      A preferred composition of the dried clear coat  
comprises from about 50% to about 70% PVDF, and from  
about 30% to about 50% acrylic resin, by weight. In  
some instances the maximum content of the PVDF component  
is about 65%, with the balance essentially comprising  
20      the acrylic resin. These solids ranges are based on the  
relative proportions of the PVDF and acrylic components  
only in the clear coat formulation. Other minor amounts  
of solids, such as UV stabilizers, block copolymers and  
compatibilizers also may be contained in the clear coat  
25      formulation.

30      In one embodiment, a successful experimental car  
body panel having exterior automotive surface properties  
was produced from a paint system in which the dried  
clear coat consisted essentially of about 50% PVDF and  
about 50% polymethyl methacrylate resin, by weight.  
This clear coat provided high gloss (after  
thermoforming) and good exterior automotive properties  
of appearance and durability. In another successful  
experimental car body panel having good exterior  
35      automotive appearance and durability properties,

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1 including gloss, the dried clear coat consisted  
essentially of about 65% PVDF and about 35% polyethyl  
methacrylate resin, by weight.

5 The acrylic resin component of the clear coat is  
desirable because of its compatibility with the PVDF in  
dry film form. The acrylic component is added to the  
PVDF in an amount that prevents deglossing of the  
finished clear coat during thermoforming. The acrylic  
resin is also added in an amount that yields a  
10 transparent clear coat in dry film form. Generally  
speaking, transparency and distinctiveness-of-image of  
the composite paint coat increase in proportion to the  
amount of acrylic resin added to the PVDF-acrylic  
system. It has been determined that a pure PVDF clear  
15 coat has reasonably good properties of durability and  
elongation, but such a 100% PVDF coating is not normally  
transparent and it deglosses excessively when heated to  
normal thermoforming temperatures. When sufficient  
acrylic resin is added to the PVDF component, the  
20 resulting clear coat becomes reasonably transparent and  
can resist deglossing at thermoforming temperatures.  
Increased transparency of the clear coat improves the  
gloss level of the finished clear coat. The acrylic  
resin is also combined with the PVDF in an amount that  
25 maintains sufficient elongation to allow the clear coat  
(and the color coat to which it is bonded) to be thermo-  
formed (as part of the laminate described below) into  
complex three-dimensional shapes, while retaining the  
exterior automotive durability properties and appearance  
30 properties, including gloss, of the finished paint coat.  
It has been determined that a dry film-form PVDF-  
acrylic-based clear coat containing more than about 35%  
acrylic resin and less than about 65% to 70% PVDF, by  
weight of the total PVDF and acrylic solids, avoids

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1 deglossing during thermoforming while achieving  
sufficient elongation.

It is believed that deglossing of a PVDF and acrylic resin-based clear coat, in some instances, can be caused by crystallization of the clear coat as it cools down after thermoforming. Greater crystallization of the PVDF-acrylic-based clear coat also is believed to be caused, at least in part, by proportionately higher thermoforming temperatures. Addition of the acrylic resin to the PVDF in the clear coat formulation may prevent crystallization of the PVDF in cool-down from thermoforming at normal thermoforming temperatures. Use of polymethyl methacrylate as the predominant component of the clear coat acrylic resin may be desirable because it produces a higher gloss level than polyethyl methacrylate. It is believed that the higher gloss results from a slower rate of crystallization of the polymethyl methacrylate during cooling. It is also believed that deglossing, in certain instances, may be caused by microcracking of the clear coat surface during thermoforming. Use of a certain amount of softer acrylic resin than polymethyl methacrylate, such as polyethyl methacrylate, may in some instances produce a high gloss surface of the clear coat after thermoforming, particularly in combination with lower thermoforming temperatures.

To the extent that deglossing of the clear coat may be caused by non-uniform coalescence of the PVDF component in the resin system, it is believed that this problem can be overcome by a more uniformly blended dispersion of the PVDF in the acrylic resin or use of a solution-based system.

The PVDF component of the clear coat is desirable because of the exterior automotive durability properties and the elongation properties it provides in the

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1 resulting clear coat, particularly in combination with  
the acrylic resin component. The PVDF component also  
provides good weatherability properties in the finished  
paint coat. It has been determined that a pure  
5 thermoplastic acrylic resin clear coat can provide good  
hardness or toughness characteristics, but it lacks  
weatherability. A pure acrylic resin clear coat also  
creates difficulties in separating from the injection  
mold after the injection-cladding step. A cross-linked  
10 thermoset acrylic resin commonly used as an exterior  
auto paint is not useful in the process of this  
invention. When thermoformed, it shatters or cracks  
when a vacuum is drawn on the laminate to which it is  
coated. A dry film-form PVDF and acrylic resin-  
15 containing clear coat having from about 30% to about 50%  
acrylic resin (by weight of the total PVDF-acrylic-based  
solids) has sufficient elongation to allow proper  
thermoforming and injection-cladding, while maintaining  
the exterior automotive durability, gloss and other  
20 appearance properties of the finished composite paint  
coat.

The color coat 46 is bonded to the clear coat after  
the clear coat has been dried on the carrier sheet. The  
color coat can be coated onto the dried clear coat, or  
25 the color coat can be coated onto a separate polyester  
casting film, dried, and later transferred from the  
casting film to the clear coat. In either case, the  
color coat is preferably applied to the casting film by  
reverse roller coating techniques similar to those  
30 illustrated in FIG. 5. A preferred dry film thickness  
of the color coat is in the range of about 0.5 to about  
1.5 mils. The color coat comprises a thermoplastic  
synthetic resinous coating composition containing a  
35 sufficient amount of pigment to provide the appearance  
necessary for exterior automotive use in the finished

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1       article. More specifically, the color coat contains a  
sufficient amount of pigment so that the composite paint  
coat maintains sufficient opacity and distinctiveness-  
of-image and avoids stress whitening throughout the  
5       thermoforming step so to function as an exterior  
automotive paint coat. The resinous material contained  
in the color coat functions in combination with the  
clear coat to produce the required exterior automotive  
surface for the finished paint coat. That is, although  
10      the clear coat provides the exterior surface portion of  
the finished paint coat, the exterior automotive  
properties of the finished surface are not controlled  
solely by the clear coat formulation. The underlying  
color coat can affect durability properties of the  
15      finished paint coat, for example. Abrasion resistance  
is an example of a mechanical property enhanced by a  
tougher color coat in combination with the exterior  
clear coat. Weatherability of the finished paint coat  
also is influenced by the color coat formulation as well  
20      as the clear coat. The color coat also comprises a  
resinous material which is capable of sufficient  
elongation at thermoforming temperatures so as to not  
disrupt the exterior automotive properties of the  
finished paint coat.

25       The color coat is preferably dried by passing it  
through the same multiple heating zones used in drying  
the clear coat. Drying temperatures in each of the  
zones are progressively increased and can be at about  
the same temperatures as those used for drying the clear  
30      coat. Preferably, similar resinous components with  
mutually compatible solvents are used in the clear coat  
and color coat so that adhesion between the clear coat  
and color coat is produced without requiring additional  
stabilizers or additives. The color coat composition is  
35      preferably a synthetic resinous coating composition

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1 having thermoplastic properties similar to the clear  
coat. Although the color coat alone does not  
necessarily require all of the exterior automotive  
properties of durability and appearance, in order to  
5 produce a useful composite paint coat, a color coat  
composition (exclusive of the pigment contained in the  
coating) having most of the desirable exterior  
automotive durability properties is preferred. In one  
embodiment, the color coat comprises a blended thermo-  
10 plastic fluorinated polymer and acrylic resin-containing  
paint system. This paint system can be similar to the  
PVDF and acrylic-based coating used in the clear coat.  
The fluorinated polymer component also can include  
copolymers and terpolymers of vinylidene fluoride. The  
15 color coat formulation can be prepared by mixing the  
acrylic component with suitable organic solvents and  
applying heat to allow the acrylic resin to dissolve.  
In a preferred embodiment the PVDF component is  
dissolved in the acrylic resin solution, although the  
20 PVDF can be maintained as a dispersion in the acrylic-  
based system. The pigment is then added to the PVDF-  
acrylic composition. Preferably, the composition of the  
dried color coat (the PVDF and acrylic-based solids,  
exclusive the pigment) comprises from about 50% to about  
25 70% PVDF and from about 30% to about 50% acrylic resin,  
by weight of the total PVDF and acrylic solids. In a  
preferred dispersion formulation, the dried color coat  
comprises about 65% PVDF and about 35% acrylic resin, by  
weight. The preferred acrylic component for the color  
30 coat is a polyethyl methacrylate resin such as Elvacite  
2042 or Elvacite 2043, or mixtures thereof. The  
relatively higher amount of PVDF in the color coat  
produces a softer film and therefore enhances elongation  
properties.

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1       The color coat may contain a substantial pigment  
level in order to provide sufficient opacity to maintain  
desirable coloration in the finished article. In a  
5       highly contoured three-dimensionally shaped article, a  
large amount of pigment may be necessary for hiding,  
following subsequent thermoforming steps. For most  
colors, a pigment level from about 3% to about 30%, by  
10      weight of the solids contained in the coating, also  
referred to as the pigment-to-binder ratio, produces the  
desired opacity in the finished paint coat. The amount  
of pigment used varies depending upon the color. For a  
red color coat used in an experimental car body panel,  
for example, a pigment level of about 23%, by weight of  
the total solids, was used. For a black color coat  
15      using carbon black pigment in an experimental car body  
panel, about 3% to 5% pigment was used.

20       The pigment contained in the color coat can affect  
exterior automotive properties. For instance, if the  
color coat is applied to a laminate as a single paint  
coat, or is applied to the laminate as an exterior paint  
coat, the pigment contained in the coating can cause the  
color coat to degloss during thermoforming of the  
laminate. (Under these circumstances, the same coating  
applied as a clear coat may not degloss during the same  
25      thermoforming step.) It has been discovered that a  
finished paint coat with a high gloss level can be  
produced with a non-deglossing exterior clear coat  
applied over a color coat which otherwise deglosses by  
itself during thermoforming. Stated another way, a  
30      color coat which normally deglosses as an exterior coat  
may be used as an underlying color coat for an exterior  
clear coat, if the clear coat can, following  
thermoforming, produce the gloss necessary for exterior  
automotive use.

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1        As to the deglossing phenomenon, it has been  
discovered that an otherwise high gloss exterior surface  
of a color coat, applied to a laminate in a flat  
(planar) coating of uniform thickness usually deglosses  
5        when the laminate is thermoformed into a complex three-  
dimensional shape. It is believed that such deglossing  
is caused by the particles added to the coating as  
pigment penetrating the exterior surface of the coating  
during the softening and elongation that occur during  
10      thermoforming. It has also been discovered that such  
deglossing can be overcome by coating (or laminating)  
the exterior clear coat over the color coat at  
sufficient film thickness that the clear coat can act as  
a barrier to prevent the color coat pigment particles  
15      from migrating from the color coat through the clear  
coat and penetrating the surface of the clear coat  
during the thermoforming step.

20      The high pigment level in the color coat also can  
affect mechanical properties of the coating, such as  
durability and elongation. Generally, the high level of  
pigment contained in the color coat reduces elongation  
of the coating. The pigment also can reduce the  
strength or hardness of the coating. A color coat which  
may, by itself, not have all of the durability  
25      properties of an exterior automotive paint coat, can  
still be useful in the finished article. However,  
elongation properties are critical because the color  
coat should not inhibit elongation of the clear coat  
during thermoforming. If the amount of PVDF component  
30      in the color coat is at least about the same or greater  
than the amount of the acrylic component in the color  
coat, elongation properties of the color coat are  
enhanced. In addition, the acrylic component of the  
color coat formulation can be a high molecular weight,  
35      high-strength resin to add back to the color coat the

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1      hardness or strength characteristics lost by the  
addition of the pigment to the color coat. The greater  
amount of PVDF in the color coat also can improve  
weatherability of the finished paint coat.

5      Thus, the desired color coat formulation provides  
the appearance and durability properties which, in  
combination with the clear coat, produce a composite  
paint coat having the properties suitable for exterior  
automotive use. The color coat also retains sufficient  
10     elongation to be thermoformed in combination with the  
clear coat so that the durability and appearance  
properties, including gloss, of the finished paint coat  
are not degraded during thermoforming. In one  
15     embodiment, an experimental car body panel was made from  
a color coat having PVDF in the range of about 50% to  
about 70%, and a high molecular weight polyethyl meth-  
acrylate resin in the range of about 30% to about 50%,  
by weight of the total (non-pigment) solids. This com-  
20     bination produced durability and appearance properties,  
including gloss, in the finished paint coat sufficient  
for exterior automotive use.

As an alternative to the PVDF and acrylic resin  
combination, the color coat also can contain other  
formulations. It is believed that a flexible pure  
25     acrylic resin with the required elongation properties,  
or certain softer acrylic copolymers or acrylic  
dispersion lacquers having sufficient elongation and  
durability properties (especially weatherability) also  
can be useful as a color coat formulation. It is also  
30     believed that certain urethanes and vinyl compositions  
such as polyvinyl chloride can provide binders for  
acceptable color coats. Use of a separate color coat  
not containing a fluorinated polymer such as PVDF can  
reduce the cost of the finished paint coat.

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1        Although the paint coat has been described in  
relation to a clear coat and a separate color coat, the  
paint coat of this invention also may be produced as a  
single pigmented thermoplastic synthetic resinous  
5        coating, with the pigment highly dispersed in the  
coating so that deglossing upon thermoforming is  
resisted. Alternatively, a clear coat having the  
required durability and appearance properties may be  
used in combination with an underlying coating or other  
10      substrate material which provides the coloration and  
other properties necessary for the combination to  
produce a finished paint coat suitable for exterior  
automotive use.

15      The size coat 47 is next coated onto the dried  
color coat, either when the color coat is coated on the  
clear coat, or when the color coat only is coated on a  
separate casting sheet. The size coat bonds the paint  
coat to the backing sheet used in the laminating step  
described below. The size coat comprises any synthetic  
20      resinous material which is heat-activated from the  
subsequent laminating step to bond the paint coat to the  
backing sheet. The preferred dry film thickness of the  
size coat is from about 0.1 to about 1.0 mil. The size  
coat is preferably applied as a thermoplastic and dried  
25      in the same multi-stage drying step used in drying the  
clear coat and the color coat. The size coat is dried  
at a temperature which evaporates the solvent without  
cross-linking the resin. The size coat composition can  
vary depending upon the composition of the color coat  
30      and the backing sheet to which the paint coat is bonded.  
For a PVDF-acrylic-based paint coat, an acrylic resin-  
based size coat is preferred for suitable bonding of the  
paint coat to the backing sheet. In one embodiment, in  
35      which the paint coat is adhered to a backing sheet made  
of acrylonitrile-butadiene-styrene (ABS), the size coat

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1 comprises a polymethyl methacrylate resin such as  
Acryloid A-101 (a trademark of Rohm and Haas Co.)  
dissolved in a suitable solvent. In another embodiment  
in which the backing sheet is a thermoplastic  
5 polyolefin, the size coat preferably comprises a  
chlorinated polyolefin.

Transfer to Thermoformable Backing Sheet

The paint-coated carrier illustrated in FIG. 4 is  
10 next laminated to a thermoformable backing sheet by dry  
paint transfer-laminating techniques. The laminating  
step is illustrated in FIG. 6. FIG. 7 schematically  
illustrates a thermoformable laminate 70 formed after  
the dry paint transfer-laminating step. The laminate 70  
15 includes the composite paint layer 44 (clear coat and  
color coat) adhered to a backing sheet 72 by the size  
coat 47. The backing sheet is preferably a semirigid,  
self-supporting, thin, flat sheet of a synthetic  
resinous material. The backing sheet is made from a  
20 material which is compatible with an injection-molded  
plastic material later used to form the structural  
substrate base of the finished article. Preferably, the  
backing sheet is made from the same or substantially the  
same polymeric material as the substrate base of the  
25 finished article. The backing sheet also is made from a  
material having a thickness capable of thermoforming  
into a complex three-dimensional shape, along with the  
adhered composite paint coat, without disrupting the  
exterior automotive properties of the paint coat. The  
30 material from which the substrate is molded can contain  
a substantial amount of filler and therefore can produce  
an imperfect surface on an article molded from the sub-  
strate material. The laminate 70 is adhered to the  
otherwise imperfect surface of the molded substrate to  
35 improve the surface characteristics of the substrate

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1 panel and produce an outstandingly smooth controlled  
exterior automotive finish. The multi-layered article  
in its finished form comprises a high performance  
essentially defect-free, three-dimensionally shaped  
5 paint coat with exterior automotive properties in  
combination with the backing sheet 72, which provides a  
buffer layer between the substandard surface of the  
substrate and the finished paint coat. The backing  
sheet material minimizes the surface imperfections  
10 transmitted to the paint coat. The preferred material  
from which the backing sheet is made is ABS. A  
preferred ABS material is Borg Warner's Cycolac L.S.  
Thermoplastic polyolefins (TPO's) including  
15 polypropylenes and polyethylenes also may be used, as  
well as polyesters or an amorphous nylon, such as Bexloy  
C-712, a trademark of DuPont. Use of TPO backing sheets  
and substrates in a composite structure is described in  
greater detail below. The thickness of the backing  
sheet can vary, but generally it is necessary for the  
20 backing sheet to have a sufficient thickness to isolate  
or absorb imperfections in the surface of the underlying  
substrate while presenting a perfectly smooth upper  
surface of the paint coat. The backing sheet is also  
not so thick that it would otherwise disrupt the  
25 elongation characteristics of the laminate during the  
subsequent thermoforming step. A desirable range of  
thickness of the backing sheet is believed to be from  
about 10 to 30-40 mils, with 20 mils being a preferred  
thickness for an ABS sheet, for example.

30 The laminating step is best understood by referring  
to the schematic view of FIG. 6, in which the paint-  
coated carrier 41 is shown stored on a top unwind roll  
74 and a flexible 20 mil thick ABS backing sheet 72 is  
stored on a bottom unwind roll 76. The paint-coated  
35 carrier, in one embodiment, comprises the clear coat and

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1 color coat on a single flexible casting sheet. The  
paint-coated casting sheet 41 is passed around a drum  
77, and the backing sheet 72 passes around a drum 78.  
The carrier and backing sheet then pass between a heated  
5 laminating drum 79 and a rubber backup roll 80. The  
laminating drum 79 is preferably made of steel and is  
preferably operated at a temperature of about 400° to  
425°F. It is pressed into contact with the overlapping  
sheets to heat them to a temperature sufficient to  
10 activate the adhesive in the size coat and press the two  
sheets into contact with each other to bond the paint  
coat to the backing sheet. The rubber backup roll 80 is  
pressed into contact with the laminating roll,  
preferably at a pressure of about 300 pounds per lineal  
15 inch. The slow speed at which the sheets travel during  
laminating ensures that the resulting laminate 70 is  
heated to a temperature approaching the temperature of  
the laminating drum. This softens the backing sheet  
material somewhat as well as activating the heat-  
20 activated size coat to ensure a complete bond between  
the paint coat and the backing sheet. The polyester  
carrier sheet of the paint-coated carrier has a heat-  
resistance well above laminating temperatures so the  
carrier sheet resists elongation during the laminating  
25 step. Following the bonding step, the flexible paint-  
coated laminate 70 is then passed around one or more  
chill rollers 82 for cooling the laminate to room  
temperature. The laminate 70 then passes onto a  
laminate rewind drum 84. The carrier sheet is stripped  
30 away from the laminate prior to the subsequent  
thermoforming step. This leaves a smooth, defect-free  
high gloss exterior surface on the clear coat which  
replicates the high gloss surface present on the carrier  
sheet.

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1        The thermoformable laminate 70 illustrated in FIG.  
7 also can be formed by separate laminating steps, each  
similar to the laminating step illustrated in FIG. 6.  
In this embodiment, a separate color coat is first  
5        transferred from a casting sheet to the backing sheet.  
The color coat may have a size coat to bond the color  
coat to the backing sheet. The casting sheet is  
stripped away after laminating. The dried clear coat is  
then transferred from a separate casting sheet to the  
10      face of the color coat opposite from the backing sheet.  
No size coat is necessary to bond the clear coat to the  
color coat during the hot laminating step.

Thermoforming

15      In the next step in the process, the laminate 70  
shown in FIG. 7 is thermoformed into a desired three-  
dimensional shape. FIGS. 8 and 9 illustrate one example  
of a thermoforming step in which the initially flat  
20      laminate can be formed into a highly contoured three-  
dimensional shape for use as the surface of a car body  
panel. Referring to FIGS. 8 and 9, separate laminate  
sheets are individually placed inside a clamping frame  
106 of a vacuum-forming machine. The clamping frame is  
movable back and forth on a track 108. The laminate  
25      sheet is initially placed in the clamping frame at the  
position shown in phantom lines at 106 in FIG. 8.

The clamping frame is then moved along the track  
into an oven 110 for heating the back sheet to a  
thermoforming temperature. An ABS backing sheet is  
heated to a temperature in the range of about 280° to  
30      about 380°F, and for Bexloy nylon the sheet is heated to  
a temperature from about 380° to about 420°F. These  
temperatures are actual sheet temperatures, not oven  
temperatures. The actual thermoforming temperatures  
35      used, within these ranges, may be a factor in preventing

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1 deglossing of the clear coat during thermoforming. In  
some instances described in the examples below, a lower  
thermoforming temperature can prevent deglossing or  
formation of small cracks in the surface of the paint  
5 coat. These phenomena may otherwise occur at higher  
thermoforming temperatures. A pressure assist can be  
used with the thermoforming step in order to reduce the  
thermoforming temperature. A lower thermoforming  
temperature of about 270°F may assist in producing  
10 higher gloss and distinctiveness-of-image in the  
finished surface. At thermoforming temperatures the  
laminate 70 sags as shown at phantom lines at the right  
side of FIG. 8.

After the laminate is heated in the oven 110 to the  
15 desired temperature, the clamping frame is moved back  
along the track, away from the oven 110 to its original  
position above a vacuum-forming buck 112. The working  
surface of the vacuum-forming buck 112 is shown in FIGS.  
20 8 and 9 as a curved surface, by way of example only.  
Other configurations can be used depending upon the  
desired three-dimensional shape imparted to the surface  
of the finished article.

The preheated laminate is next vacuum-formed into  
the desired three-dimensional shape by first drawing a  
25 vacuum on the vacuum-forming buck 112 through its  
connection 114 to a vacuum pump. The vacuum-forming  
buck 112 is then raised to the position shown in FIG. 9,  
where it has risen into the clamping frame. The vacuum  
is pulled through holes in the buck to force the molten  
30 plastic into the shape of the working surface of the  
buck. Positive air pressure can be applied to the free  
face of the clear coat on the opposite side of the back  
to increase forming pressure. The buck stays in place  
long enough to cool the plastic to a solid state again  
35 before the buck drops away back to the position shown in

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1 FIG. 8. This leaves behind the plastic in the shape of  
the buck. The preferred vacuum-forming step is to use a  
male vacuum former in which the vacuum-forming buck 112  
is in direct contact with the backing sheet so as to not  
5 contact the exterior clear coat 45 on the opposite side  
of the backing sheet. In this way, the backing sheet  
hides most of any of the possible defects in the working  
surface of the buck; and the surface of the clear coat  
is not affected, but is allowed to elongate freely.

10 In an alternate thermoforming step (not shown), the  
laminate 70 can be fed to the thermoformer as a  
continuous sheet. The laminate first passes through the  
oven and then passes to the thermoforming buck in line  
with the downstream end of the oven. The continuous  
15 sheet is stopped at preset intervals for heating the  
laminate to the thermoforming temperature while a  
previously heated portion of the sheet is vacuum formed  
into the desired shape.

20 The thermoforming step produces a three-  
dimensionally shaped preformed laminate 116 illustrated  
in FIGS. 10 and 11. For simplicity, the preformed  
laminate is illustrated as comprising the backing sheet  
72 and the composite paint coat 44 adhered to it. The  
laminate is illustrated in a three-dimensionally shaped  
25 form following the thermoforming step as one example  
only of a possible three-dimensional shape. Other  
complex three-dimensional shapes are also possible. The  
composite paint coat resists elongation greater than  
about 40% during thermoforming without deglossing,  
30 cracking, stress-whitening, or otherwise appreciably  
disrupting the exterior automotive durability and  
appearance properties that were present in the composite  
paint coat before thermoforming.

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1        Bonding of Thermoformed Laminate to Substrate Panel

FIGS. 10 and 11 schematically illustrate steps in a subsequent injection-cladding operation in which the preformed laminate 116 is adhered to an underlying plastic substrate panel. The injection-cladding step is an example of a possible means for adhering the laminate to the substrate. Following the thermoforming step, the laminate is placed in an injection mold 117 and fused to the face of an injection-molded substrate 118. FIG. 10 illustrates a first step in the injection-cladding step in which a plastic injection mold is in its open position, and the preformed laminate 116 is placed in the mold cavity between front and rear mold halves 120 and 122. The inside surface 124 of the mold half 120 identically matches the exterior contour of the paint-coated surface of the preformed laminate. This surface 124 of the mold is a rigid, high gloss, highly-polished surface which is free of surface defects so that surface defects are not transferred to the high gloss, clear-coated surface of the laminate. After the laminate is preformed to its desired shape, it is trimmed to size and is ready for injection-cladding. The vacuum-formed die cut sheet is placed inside the injection mold and the mold halves 120 and 122 are closed, leaving a space of the desired size behind the laminate for receiving the injection molding material. As shown best in FIG. 11, the injection molding material 118 flows through a passage 126 in the rear mold half 122 and into the mold cavity behind the preformed laminate 116. The molding material conforms to the shape of the mold cavity and is permanently fused to the backing sheet portion of the laminate. The injection molding material does not come into contact with the paint coat. As described previously, the molding materials from which the substrate 118 and the backing sheet 72 are made are

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1 compatible so that the two materials fuse to form an integral molded substrate on which the paint coat provides a defect-free finish. The temperature at which the injection-mold is operated is substantially below  
5 the melt temperature of the molding material. In one embodiment, in which an ABS backing sheet is used, the molten material is at a temperature of about 450°F, for example. A water jacket can be used to cool the faces of the mold. During injection-molding, the backing sheet material softens when fusing to the injection molding material, and the surface of the clear coat replicates the surface of the mold, owing to the pressure from the molding operation. Both faces of the mold are cooled to a temperature in the range of about  
10 160° to 170°F, so that the paint coat 44 on the laminate remains stable during injection molding. The clear coat material at the time of injection molding has had all of its solvent gas removed so that evolution of gases during injection molding is essentially avoided. As a result, the clear coat retains its high gloss surface characteristics during the injection molding step.

FIG. 12 schematically illustrates the finished article 130 produced by the process of this invention. In the finished article, the preformed laminate and its backing sheet have been fused to the molded substrate 118. In one embodiment, the article can be an exterior car body member or panel. The exterior clear coat 45 and the color coat 46 combine to produce a paint coat with exterior automotive properties on the surface of the substrate. Any defects in the substrate material have been absorbed by the 20 mil thick backing sheet 72 to provide a defect-free paint coat.

Alternatively, the color coat may in some instances be eliminated or the pigmentation reduced, and the coloration may be provided by pigments contained in the

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1       backing sheet or molding material for the substrate. In  
these instances, the clear coat is used with the backing  
sheet which is thermoformed and then adhered to the  
substrate according to the processing techniques  
5       described previously. As one advantage, coloration  
contained in the backing sheet can hide the effects of  
chipping of the paint coat.

10      Although the invention has been described with  
respect to the injection-molding steps illustrated in  
FIGS. 10 and 11, other techniques can be used for  
forming the finished article illustrated in FIG. 12.  
These include, but are not limited to, use of sheet  
molding compound (SMC), compression cladding and  
reaction injection molding (RIM) techniques, and  
15      pressure-sensitive or adhesive bonding techniques.  
Other plastic molding materials also can be used in  
place of ABS for fusing the substrate panel to the  
paint-coated backing sheet. These may include thermo-  
plastic polyolefins (TPO's) such as polypropylenes and  
20      polyethylenes; polyesters; and amorphous nylon. In  
these instances, the backing sheet is preferably made  
from the same polymeric material as the injection  
molding material.

25      Characteristics of Finished Paint Coat

The following is a list of physical properties  
which are used herein to measure whether the finished  
paint coat is useful as an exterior automotive paint  
coat:

30           (1) Gloss  
              (2) Distinctiveness-of-Image  
              (3) Color Uniformity (hiding ability)  
              (4) Dry Film Thickness Uniformity  
              (5) Gasoline Resistance  
35           (6) Solvent Resistance

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1                   (7) Acid Spotting Resistance  
                  (8) Hardness  
                  (9) Abrasion Resistance  
                  (10) Impact Strength  
5                   (11) Adhesion of Paint Coat  
                  (12) Accelerated UV Resistance  
                  (13) Resistance to Water and Humidity Exposure

10                 Properties (1) through (4) are considered appearance properties and properties (5) through (13) are considered durability properties. Specifications and test methods for each of these physical properties are described below. Certain specifications and test methods identified below are defined by publicly available standard industry specifications and test methods which are incorporated herein by this reference.

15                 (1) Gloss is measured by specular reflectance of a beam of light at angles of 20° and 60°. The desired specular reflectance for an exterior automotive paint coat surface is at least about 60 to 65 gloss units at 20°, and at least about 75 to 80 gloss units at 60°. Specular reflectance and other criteria herein are measured before the finished painted surface is buffed and waxed. A preferred test method is described in GM 20 Test Specification TM-204-A. The Byk-Mallinckrodt "multigloss" or "single gloss" gloss meters can be used for measuring specular gloss of the finished surface. These gloss meters give values equivalent to those obtained from ASTM Method D-523-67. Either gloss meter 25 is used with gloss standards covering the expected range of measurement, together with a piece of polished black glass plate of known refractive index. The gloss meter is calibrated by setting it to read the gloss of a highly polished standard and then reading the gloss of a 30 working standard having a value preferably in the range 35

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1       of the test panel. The second standard should agree  
within one unit of its assigned value. At least two  
readings are taken on a different area of the test  
panel. These values are averaged if they agree within  
5       one unit. If the range is larger than one unit,  
additional regions are taken and a mean value is  
calculated.

10      (2) Distinctiveness-of-Image (DOI) is a  
measurement of the clarity of an image reflected by the  
finished surface. DOI can be measured from the angle of  
reflection of a light beam from a spherical surface.  
The desired DOI for an exterior automotive paint coat  
surface is at least about 60 units, where 100 units is  
15      the maximum DOI reading. DOI is measured by the  
Hunterlab Model No. D47R-6F Dorigon Gloss Meter. A test  
panel is placed on the instrument sensor and the  
sharpness of the reflected image is measured. Details  
of the DOI test procedure are described in GM Test  
Specification TM-204-M, which are incorporated herein by  
20      reference.

25      (3) Color Uniformity is a test to determine  
whether coloration of the paint coat remains uniform  
after thermoforming and injection-cladding. Coloration  
is tested after the paint coat is coated on the casting  
sheet, before transfer to the backing sheet. Coloration  
testing is repeated after a deep draw stretch simulating  
elongation during thermoforming, to determine whether  
the color has changed. A desirable coloration  
uniformity can be a color change of no greater than  
30      about one to two McAdam units on a colorimeter.

35      (4) Dry Film Thickness (DFT) is a standard  
industry measurement of the film thickness of the  
finished paint coat, to determine whether the paint coat  
thickness matches a required film thickness specified by  
the auto manufacturer. For the present exterior

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1        automotive specifications, uniformity of the finished  
paint coat is determined to be a more useful parameter  
in determining whether the paint coat meets appearance  
requirements. Thickness uniformity of the finished  
5        paint coat can be measured from several locations on the  
finished article, including highly contoured areas, to  
determine whether variations in the thickness of the  
finished paint coat exceed a desired level.

10      (5) Gasoline Resistance requires no color change,  
degradation, tackiness, marring or loss of paint  
adhesion on plastic parts used on and adjacent to fuel  
filler openings after being immersed for ten seconds,  
ten times, in a specified reference fuel with a 20  
second dry off period between each immersion.  
15      Immediately after the tenth immersion, the painted  
surface is checked and must pass Thumbnail Hardness  
according to GM Test Specification TM 55-6, incorporated  
herein by reference..

20      (6) Cleanability is tested according to GM Test  
Specification TM 31-11 which is incorporated herein by  
reference. According to this test, the painted plastic  
part is required to withstand ten rubs with cheesecloth  
saturated with 9981062 Naphtha or currently used and  
approved cleaning solvents, with no evidence of  
25      staining, discoloration, or softening of the painted  
surface. This test requires no evidence of color  
transfer from the test part to the cloth. One rub  
consists of one forward and backward motion.

30      (7) Acid Spotting Resistance requires the test  
part to withstand exposure to 0.1 N sulfuric acid for 16  
hours without any evidence of staining, discoloration,  
or softening of the painted surface.

35      (8) Hardness is measured by a standard Knoop  
Hardness Test. The required hardness is at least a  
Knoop hardness number of four.

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1                     (9) Abrasion Resistance is tested by a  
gravelometer under the standard test method identified  
as SAE J-400. According to this test, the painted part  
shall withstand the Gravelometer Test at minus 10°F with  
5                     a minimum rating of eight (F.B. Gravelometer Rating  
Chart). The tested part should withstand the  
Gravelometer Test as-received and after Florida exposure  
described below. A Fisher Body Material Specification  
FBMS 26-7 (incorporated herein by reference) also  
10                  defines a minimum level of wear resistance for the  
finished paint coat.

15                  (10) Impact Strength is tested at room temperature  
by the Gardener Test and by the Rosand Test at minus  
20°F. The paint coat should withstand at least 20 inch-  
pounds of direct impact with no failure.

20                  (11) Paint Adhesion is tested by a standard Tape  
Adhesion Test described in GM Test Specification TM  
55-3, which is incorporated herein by reference.  
According to this test, a tape is pressed down over an  
X-shaped cut in the paint coat and the tape is then  
removed to test the amount of peeling. The Adhesion  
Test requires a minimum of 99% of the paint remaining in  
the tape test area.

25                  (12) Accelerated UV Resistance, also referred to as  
Accelerated Weathering, or QUV, measures the  
weatherability of a paint coat in accelerated test  
procedures designed to provide an accurate indication of  
long-term UV resistance or other weatherability  
properties. According to a QUV test useful for  
30                  measuring accelerated UV Resistance, the test panel  
should not show any significant surface deterioration or  
embrittlement, loss of coating adhesion, objectionable  
shrinkage, or noticeable color or gloss change after  
about 500 to 1,000 hours exposure to UV light and

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1        condensation apparatus per ASTM G-53 using eight hour UV  
cycle at 70°C and four hour humidity cycle at 50°C.  
5        (13) Resistance to Water and Humidity Exposure is measured by several tests. According to a first test,  
10      the finished part shall withstand 96 hours of humidity exposure at 100% relative humidity and 100°F in a humidity cabinet defined in GM test specification TM 55-3, and a two-hour water immersion test at 100°F according to GM test specification TM 55-12. These test specifications are incorporated herein by reference. The resulting test panel should show no evidence of blistering when examined one minute after removal from the test cabinet and shall withstand the Paint Adhesion Test described above. The Paint Adhesion Test is performed within one minute after removal from either test cabinet. In a second test, the finished part should withstand 15 cycles of the Moisture-Cold Cycle Test defined in GM test specification TM 45-61A (incorporated herein by reference), without any visible signs of cracking or blistering. After 15 cycles, the part shall withstand 96 hours of the humidity exposure described above, followed by passing the Paint Adhesion Test also described above. The Paint Adhesion Test is performed within one minute after removal from the humidity environment. One cycle consists of 24 hours and 100% relative humidity at 100°F, 20 hours at minus 10°F, and four hours at room temperature.  
15      Other durability tests can be used to determine the usefulness of a paint coat for exterior automotive applications. These tests can include long-term ultra-violet radiation exposure and heat exposure tests. Both of these tests require long-term exposure of the panel to the particular environment. For instance, one long-term UV test can require two years exposure to determine the long-term resistance of the paint coat to  
20       
25       
30       
35

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1 ultraviolet radiation. In a long-term weathering and  
heat resistance test, the painted plastic part is  
required to withstand two years direct Florida and  
Arizona test site exposure without any significant color  
5 or gloss change, loss of adhesion, or other detrimental  
surface or substrate deterioration effects. After long-  
term Florida and/or Arizona exposure, painted samples  
must withstand testing under the Tape Adhesion,  
Abrasion, Gravelometer and Moisture-Cold Crack Cycling  
10 tests. Five years Florida and Arizona test site  
exposure also can be used. Other test methods can  
include sulfide staining, detergent resistance, solvent  
resistance, compatibility, cycle tests, humidity and  
adhesion, humidity and wear resistance, cold exposure,  
15 and Florida and Arizona exposure tests set forth in FBMS  
26-7.

Example 1

20 A high gloss jet black laminated exterior  
automotive paint coat was formed on the exterior surface  
of an experimental plastic rear window molding for a  
Pontiac Grand AM. The window molding was similar to  
that shown in FIG. 2. The paint coat was first coated  
25 onto a surface of a flexible polyester film casting  
sheet. The flexible carrier comprised two mil thick  
high gloss American Hoechst 3000 polyester film. The  
paint coat comprised a clear coat, a color coat, and a  
size coat coated onto the polyester film casting sheet  
in that order. A thin film of wax was first coated on  
30 the polyester film. The wax coating formulation  
comprised, on a weight basis, 40% xylene, 59.4%  
cyclohexanone, and 0.6% carnauba wax. The wax was  
dissolved in the solvents at 120°F and cast on the  
polyester film using a gravure coating cylinder. The  
wax coating was applied as a thin film approximately  
35

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1        0.001 mil thick. The wax-coated casting sheet was then  
passed through a drying oven and dried at 250°F with a  
line speed of 25 feet per minute. The wax-coated  
5        casting sheet could be separately run at a higher lineal  
speed, if desired. The wax film did not affect  
replication of the polyester film surface by the clear  
coat.

The clear coat was then prepared from the following  
formulation:

	<u>Ingredient</u>	<u>Parts</u>
10	BLO (Butyrolactone)	15.00
	DIBK (di-isobutyl ketone)	27.00
	Polymethyl methacrylate (Elvacite 2010)	18.00
15	PVDF (Kynar 301F)	18.00
	BLO	6.28
	Cyclohexanone	15.00
	Silicone fluid (Dow Corning DC-11)	0.72

20        The Elvacite 2010 acrylic resin was mixed with the  
BLO and DIBK solvents under heat applied at  
approximately 130°F to dissolve the acrylic resin in the  
solvents. The resulting mixture was then allowed to  
cool over night. The PVDF, together with the remainder  
25        of the BLO and cyclohexanone solvents and the silicone  
fluid, were then mixed at room temperatures so that the  
PVDF component remained as a dispersion in the mixture,  
rather than dissolving. The dried clear coat contained  
30        approximately 50% PVDF and 50% polymethyl methacrylate,  
by weight, based on the total PVDF-acrylic solids.

35        The clear coat was coated on the casting sheet in a  
dry film thickness of about 0.8 mil. The clear coat was  
applied to the sheet by a reverse roll coater  
(illustrated in FIG. 5) in line with the gravure oven  
previously used for drying the wax film, so that the

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1      clear coat was applied directly after drying of the wax.  
The clear coat was dried on the carrier sheet by passing  
it through a multi-zone impinging air drying oven having  
three heating zones spaced apart axially along the  
length of the carrier, with each drying zone having a  
progressively higher temperature. The clear-coated  
carrier was passed through the heating zones at a line  
speed of 25 feet per minute and each heating zone was 40  
feet long. Temperatures of the three heating zones  
were: Zone 1: 260°F, Zone 2: 330°F, Zone 3: 390°F.  
Passing the clear coat through the three heating zones  
removed substantially all solvent gases from the clear  
coat to produce a dry clear coat of uniform film  
thickness.

15     A jet black color coat was next coated on the dried  
clear coat at a dry film thickness of about 0.8 mil.  
The color coat formulation was as follows:

	<u>Ingredient</u>	<u>Parts</u>
	Cyclohexanone	9.27
20	DIBK	18.54
	BLO	8.34
	Polyethyl methacrylate (Elvacite 2042)	10.02
	Dispersing agent (Solsperse 17,000)	0.10
25	PVDF (Kynar 301F)	24.04
	BLO	14.14
	Black Dispersion	15.00

30     The black dispersion comprised carbon black in a  
vehicle of Elvacite 2043, available commercially as  
Gibraltar 438-39110 pigment. The color coat formulation  
was prepared in a similar manner to the clear coat  
formulation in that the acrylic resin was first  
dissolved in the cyclohexanone, DIBK and BLO solvents at  
35     a temperature of about 130°F and was then allowed to

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1 cool before the PVDF component was added to the mixture  
to form a dispersion of the PVDF in the acrylic resin.  
The pigment was then added to the resulting mixture to  
produce a jet black color. On a weight basis, the  
5 amount of pigment contained in the color coat  
formulation was about 4% to about 5%. The dried color  
coat comprised approximately 65% PVDF and approximately  
35% acrylic resin, by weight of the total PVDF and  
acrylic (non-pigment) solids. The acrylic resin  
10 component comprised polyethyl methacrylate comprised of  
approximately 90% Elvacite 2042 and approximately 10%  
Elvacite 2043. The color coat was coated onto the dried  
clear coat in liquid form and then passed through the  
three stage oven described above to dry the color coat.

15 A size coat was next prepared for use with an ABS  
backing sheet. The size coat comprised 50 parts methyl  
methacrylate resin known as Acryloid A-101 (a trademark  
of Rohm and Haas Co.) dissolved in 50 parts methyl-  
ethyl-ketone solvent. The size coat was coated onto the  
20 dried color coat in a dry film thickness of about 0.1  
mil using a single station gravure coating cylinder.  
The size coat was then dried by passing it through a  
single stage drying oven at a temperature of about  
275°F.

25 The resulting paint-coated carrier was then passed  
to a laminating operation similar to that illustrated in  
FIG. 6, where the paint coat was transferred from the  
polyester carrier to a 20 mil thick ABS backing sheet.  
In the laminating operation, the backing sheet and the  
30 paint-coated carrier were run at a lineal speed of 15  
feet per minute, and the laminating drum was operated at  
a temperature of 400°F. The size coat was heat-acti-  
vated and the paint coat was transferred from the  
carrier to the face of the ABS backing sheet during the  
35 laminating operation, in which the hot steel drum

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1 applied a force of about 300 pounds per lineal inch.  
The polyester carrier film was stripped away from the  
surface of the laminate, leaving the paint coat bonded  
to the ABS sheet, with the clear coat providing a high  
5 gloss surface on the exterior of the ABS backing sheet.

The paint-coated laminate was then thermoformed  
into a complex three-dimensional shape to form the  
plastic window molding. The laminate was thermoformed  
10 by first heating the flat laminate in an oven to a  
temperature of about 360°F, to soften the laminate.  
After the laminate was heated, it was placed over a  
vacuum-former buck similar to that shown in FIGS. 8 and  
15 9, and a vacuum was drawn against the buck on the ABS  
side of the laminate to form the heated laminate into  
the three-dimensional shape of the window molding.

The thermoformed laminate was then trimmed to fit  
in the mold cavity of a plastic injection molding  
machine. An ABS plastic molding material, for forming  
20 the substrate base of the window molding, was injected  
into the mold behind the thermoformed laminate to fuse  
the ABS molding material to the laminate. The mold was  
operated at normal melt temperature for the ABS resin.  
This formed a window molding as a integral plastic part  
25 with a defect-free, paint coat on the exterior surface  
of the panel.

The window panel was tested and the tests  
demonstrated the usefulness of the paint coat as an  
exterior automotive paint coat. The test results  
indicated that desirable appearance properties,  
30 including gloss, were produced. Gloss measured 62 units  
at 20° and 79 units at 60°. DOI measured 64. Color  
uniformity was good. The test results also demonstrated  
a desirable combination of durability properties. The  
test panel passed gasoline resistance, acid resistance,  
35 abrasion resistance (gravelometer reading of 8), impact

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1        resistance (80 in-lb. for Gardner Test), QUV, and 96-hour humidity exposure tests, according to test methods similar to those described above.

5        Example 2

10      A high gloss red laminated exterior automotive paint coat was formed on the exterior surface of a highly contoured plastic automobile body panel. The laminate was matched to a General Motors Fiero red body color and used to make a prototype injection-clad Fiero rear quarter panel. The paint coat was first coated onto a casting film comprising a two mil thick high gloss American Hoechst 3000 polyester film. A clear coat, color coat, and size coat were coated onto the casting film in that order. The clear coat was prepared from the following formulation:

	<u>Ingredient</u>	<u>Parts</u>
	Cyclohexanone	15.47
20	BLO (Butyrolactone)	7.52
	DIBK (di-isobutyl ketone)	21.66
	Polyethyl methacrylate (Elvacite 2042)	12.95
	UV absorbers	1.1
25	PVDF (Kynar 301F)	24.05
	BLO	17.24

30      The Elvacite acrylic resin was dissolved in the BLO, DIBK and cyclohexanone solvents, while mixing and under heat at approximately 130°F. The resulting mixture was allowed to cool overnight. The UV absorbers were then added to the mixture and the PVDF was dispersed in the resin. The remaining BLO solvent was added to dilute the final mixture. The PVDF component remained as a dispersion in the mixture rather than dissolving. The dried clear coat contained approxi-

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1 mately 65% PVDF and 35% acrylic resin, based on the  
total PVDF and acrylic solids.

5 The clear coat was coated on the casting film in a dry film thickness of 0.6 mil. The wax coat described in Example 1 was omitted in this test. The clear coat was dried on the casting sheet by passing it through the same three-zone drying oven described in Example 1. Line speed and temperatures of the three zones were the same. Passing the clear coat through the drying oven removed substantially all solvent gases from the clear coat and produced a dry clear coat of uniform film thickness.

10 A red color coat was next coated on the dried clear coat at a film thickness of about 0.8 mil. The color coat formulation was as follows:

	<u>Ingredient</u>	<u>Parts</u>
	Cyclohexanone	10.61
20	Polyethyl methacrylate (Elvacite 2042)	2.99
	Dispersing agent (Solsperse 17,000)	0.10
	PVDF (Kynar 301F)	19.95
	BLO	4.02
	Solvent (M-Pyrol)	8.45
25	Red Dispersion	57.9

30 The dispersion comprised several pigments as a powder mixed in a vehicle comprising polyethyl methacrylate resin, Elvacite 2043, 16% solids, and 84% cyclohexanone solvent. The color coat formulation was prepared in a similar manner to the clear coat formulation, in that the acrylic resin was first dissolved in the solvents at a temperature of about 130°F. The dispersing agent and a portion of the red dispersion were added. The mixture was allowed to cool

35

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1 to room temperature and the PVDF component was dispersed  
using a high speed mixer. The remainder of the red  
dispersion was then added to the resulting mixture to  
produce a red color match. The dried color coat  
5 comprised approximately 65% PVDF and approximately 35%  
acrylic resin, by weight of the total PVDF and acrylic  
(non-pigment) solids. The acrylic resin component com-  
prised polyethyl methacrylate, approximately 80%  
Elvacite 2043 and approximately 20% Elvacite 2042. The  
10 pigment was present in a ratio of three parts pigment to  
ten parts resin binder, or approximately 23% of the  
total solids. The color coat was coated onto the dried  
clear coat in liquid form and then passed through the  
15 three-stage oven described above for drying the color  
coat.

A size coat was next prepared for use with an ABS  
backing sheet. The size coat comprised 75 parts methyl  
methacrylate resin, Acryloid A-101, dissolved in 25  
parts toluene solvent and mixed until homogeneous. (The  
20 Acryloid A-101 comprised 40% PMMA solids in MEK  
solvent.) The size coat was then coated onto the dried  
color coat in a film thickness of about 0.1 mil. The  
size coat was applied by a reverse roll coater similar  
to that described in FIG. 5 and was then dried in the  
25 same three-stage drying oven as the clear coat and the  
color coat. The resulting paint-coated carrier was  
transferred to a laminating operation similar to that  
illustrated in FIG. 6, where the paint coat was  
transferred from the polyester carrier to a 20 mil thick  
30 ABS backing sheet. The carrier film was stripped away  
from the surface of the laminate, leaving the red paint  
coat with a high gloss surface on the exterior of the  
ABS backing sheet.

The laminate was then thermoformed into the complex  
35 three-dimensional shape of the rear quarter panel. The

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1      laminate was thermoformed by passing it, as a continuous  
sheet, through an oven for heating the laminate to a  
temperature of about 290°F. After the continuous sheet  
was heated to this temperature, it was then moved over a  
5      vacuum-former and a vacuum was drawn to form the  
laminate into the three-dimensional shape of the rear  
quarter panel. Positive air pressure of 15 psi was  
applied to the clear-coated free face of the sheet and  
the vacuum was drawn on the ABS side of the sheet..

10     The thermoformed laminate was placed in the mold  
cavity of a plastic injection mold, and an ABS-based  
plastic molding material for forming the substrate base  
of the quarter panel was injected into the mold behind  
the thermoformed laminate, to fuse the molding material  
15     to the ABS side of the laminate. This formed the rear  
quarter panel as an integral plastic part with a defect-  
free, glossy paint coat on the exterior surface of the  
panel.

20     The panel was tested, and the tests demonstrated  
the usefulness of the paint coat as an exterior  
automotive paint coat. The test results indicated that  
desirable appearance properties, including gloss, were  
produced. Gloss measured 65 units at 20° and 80 units  
at 60°. DOI measured 65. Color uniformity was good.

25     The test results also demonstrated a desirable  
combination of durability properties. The test panel  
passed gasoline resistance, cleanability, acid  
resistance, hardness (7-8 reading on Knoop hardness  
scale), abrasion resistance (gravelometer reading of 8),  
30     impact resistance (80 in-lb. for Gardner Test), QUV, and  
96-hour humidity exposure tests, according to test  
methods similar to those described above. Florida  
exposure passed after three months.

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1       Example 3

Tests were conducted to determine the relative proportions of the PVDF and acrylic components of the clear coat and the color coat capable of producing a composite paint coat that can be cast as a film, laminated to a backing sheet, thermoformed, and injection-clad to form a finished article with an exterior automotive paint coat surface. In this example, standard spray type automotive acrylic enamel paints manufactured by DuPont were used as a paint coat in the process of this invention. These types of paint systems are commonly used at present as exterior automotive paint. The paint coats were thermoset and they cross-linked at low temperatures on the carrier when dried. These paint coats were then transferred from the carrier to a 20 mil thick ABS backing sheet which was then drawn on a vacuum-former. The paint coat was too brittle to elongate properly; it cracked and shattered at stress points in the laminate when thermoformed.

Similar DuPont urethane-based automotive paints normally used on rubber bumpers also failed in a similar manner when thermoformed. These paint systems were stable at room temperature but they cracked during high temperature vacuum-forming.

Example 4

In a test similar to that described in Example 3, a non-thermoset acrylic lacquer paint coat was evaluated. The paint coat comprised a DuPont lucite dispersion lacquer thermoplastic acrylic resin paint system. The paint coat was coated on a casting sheet, dried, and laminated to a 20 mil thick ABS backing sheet. This paint system could be thermoformed, but it was difficult to process. If used as a high-solids (low solvent)

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1        paint coat, the lacquer took too long to dry. If  
stabilizers were added to improve drying, it cracked  
when thermoformed. It also tended to adhere to the  
injection mold.

5

Example 5

10      Other pure thermoplastic acrylic resin paint  
systems were tested, such as a polymethyl methacrylate  
and solvent-based paint coat with dispersed pigments.  
Such pure acrylic paint systems were characterized  
primarily by their difficulty in processing because of  
their slow rate of solvent evaporation during drying and  
a tendency to adhere to the surface of the injection  
mold. Acrylic paint systems with appreciable amounts of  
15      pigment deglossed during thermoforming. Pure  
thermoplastic acrylic paint systems also tended to lack  
certain mechanical properties that did not meet exterior  
automotive criteria, including low abrasion resistance  
(gravelometer) properties. In addition, these pure  
acrylic resin formulations did not cast well in film  
20      form because of their tendency to adhere too strongly to  
the casting sheet.

25

Example 6

A pure PVDF (Kynar 301F) paint system was tested in  
the process of this invention. The PVDF paint system  
had sufficient elongation to thermoform properly without  
cracking, but it deglossed excessively during  
thermoforming.

30

Example 7

35      A thermoplastic acrylic-vinyl paint system was  
tested experimentally according to the process of this  
invention. The paint system also included a dispersed  
black pigment, about 3% by weight of the total solids.

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1        This paint system had been used successfully previously  
for interior automotive trim parts on dashboard panels  
and the like. The paint system could be laminated to an  
5        ABS backing sheet, but when it was thermoformed, it  
deglossed excessively. This interior paint system did  
not produce an exterior automotive paint surface that  
meets minimal gloss and DOI specifications for exterior  
automotive use. This paint coat, when used for auto-  
10      matic interior parts, also is not applied with a film  
thickness necessary to meet durability specifications  
for an exterior automotive finish. Using the higher  
level of pigment required for an exterior automotive  
paint coat produced extreme deglossing during thermo-  
forming. Other mechanical properties necessary for  
15      exterior use also were not present.

Example 8

20       A blended thermoplastic PVDF-acrylic paint system  
was tested experimentally with the process of this  
invention. This blended paint system comprised a  
dispersion of 72% PVDF and 28% acrylic resin, by weight  
of the total PVDF-acrylic solids. This paint system was  
similar to one used commercially on exterior metal trim  
parts for automobiles in which the metal was spray  
painted and then cold-formed to produce the desired trim  
25      part. This blended paint system contained a dispersion  
of black pigment comprising about 3% by weight of the  
total solids. This paint system was not suitable for  
exterior automotive use. The paint system could be  
laminated to an ABS backing sheet, but when  
30      thermoformed, it deglossed excessively. In addition to  
its low gloss, this paint system also did not possess  
the exterior DOI requirements for an exterior automotive  
finish.

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1       Example 9

A PVDF and acrylic resin clear coat was tested in combination with a pure acrylic-based color coat. Each paint coat was coated on a casting sheet, the coatings were dried and transferred to an ABS backing sheet to form a composite paint coat, and the sheet was thermo-formed. In one test, the acrylic resin component in the color coat comprised an outdoor weatherable acrylate known as Korad D, a product of Polymer Extruded Products of Newark, New Jersey. Other tests were conducted with pure acrylic color coat formulations comprising PMMA and PEMA copolymers. In one test, the color coat comprised a pure Elvacite 2042 polyethyl methacrylate. Visual observation of the thermoformed laminates indicated that good appearance properties, including gloss and DOI, were achieved. One observation was that a PVDF and acrylic clear coat can be used in combination with a color coat not containing the PVDF component, resulting in a less expensive composite paint coat that eliminates the more expensive fluorocarbon component from a portion of the finished paint coat.

Example 10

Tests were conducted on a composite paint coat comprising an exterior clear coat bonded to a color coat. The solids in the clear coat and the color coat both consisted essentially of a blended thermoplastic PVDF-acrylic paint system. The paint coat was coated on a casting sheet, transferred to an ABS backing sheet, thermoformed, and injection-clad to an ABS substrate. It was determined that certain PVDF/acrylic ratios in the clear coat did not produce a sufficient combination of the appearance and durability properties in the finished laminate suitable for exterior automotive use. For instance, 100% PVDF deglossed during thermoforming,

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1 whereas 100% acrylic resin created processing problems,  
including adherence to the injection mold and slow  
solvent evaporation. FIG. 13 shows a graph representing  
5 a performance curve for the PVDF-acrylic based composite  
paint coat. This curve represents the relationship  
between gloss (gloss units at 60°) of the clear coat on  
the finished article and the ratio of PVDF to acrylic in  
the dried clear coat, by weight of the total PVDF and  
acrylic-based solids. This curve is based upon  
10 experimental evaluations of clear coat formulations  
comprising PVDF and various acrylic resin combinations,  
primarily combinations of polymethyl methacrylate and  
polyethyl methacrylate, or mixtures thereof, including a  
range of low to very high molecular weight acrylic  
15 resins. This curve illustrates that a transition point  
exists between acceptable gloss and unacceptable  
deglossing above about 65% to 70% PVDF in the clear coat  
formulation. If the PVDF is contained in a formulation  
greater than about 70%, excessive deglossing is produced  
20 upon thermoforming. The tests used to determine the  
performance curve also revealed that a 50/50 ratio of  
PVDF to acrylic is approximately where addition of a  
greater proportion acrylic resin makes processing of the  
paint system too difficult. The lined portion of the  
25 curve represents a workable combination of PVDF and  
acrylic resin, for these particular resin combinations,  
to produce a clear coat having a desirable gloss level.  
The minimum desired gloss level, for the purpose of this  
example, was selected as 75 units for 60° specular  
30 reflectance. These tests have shown that polymethyl  
methacrylate in the PVDF and acrylic paint system can  
produce a generally higher gloss level than polyethyl  
methacrylate; and therefore, the curve illustrated in  
FIG. 13 will tend to rise as proportionately more  
35 polymethyl methacrylate is used. The curve will become

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1 lower as more polyethyl methacrylate is used. Moreover,  
the tests have shown that addition of pigment to the  
underlying color coat may cause greater deglossing of  
the exterior clear coat during thermoforming; and there-  
5 fore, the curve illustrated in FIG. 13 will tend to  
become lowered as the pigment level in the color coat  
increases. Tests have also shown that deglossing of the  
clear coat may be caused by several factors. For  
instance, if the clear coat is too thin, the pigment  
10 particles from the underlying color coat may migrate  
through the surface of the clear coat upon thermoforming  
and cause at least some deglossing. In certain  
instances, a thicker clear coat can resist this type of  
deglossing. However, in other instances, a thicker  
15 clear coat does not prevent deglossing. In one test, a  
relatively thick (1.2 mil) clear coat comprising 50%  
PVDF and 50% polymethyl methacrylate deglossed when  
thermoformed at 340°F. The underlying color coat  
contained a substantial pigment level of 23%. By  
20 increasing the PVDF in the clear coat to 65% solids and  
by changing the acrylic component to 35% polyethyl meth-  
acrylate, and by using a lower thermoforming temperature  
of 290°F., deglossing of the clear coat was prevented.

25 Example 11

Experiments were conducted to compare the physical  
properties of exterior automotive PVDF/acrylic coatings  
prepared as a solution of PVDF in the acrylic resin with  
similar dispersion systems. The tests were conducted  
30 for both the clear coat and the color coat to compare  
gloss and distinctiveness-of-image (DOI) levels for  
thermoformed panels made with combinations of both  
solution and dispersion cast PVDF/acrylic films.  
Dispersion and solution clear coats and color coats were  
35 produced from the following formulations:

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**1      Dispersion clear coat:**

	<u>Ingredient</u>	<u>Parts</u>
	Polymethyl methacrylate (Elvacite 2010)	50
5	PVDF (Kynar 301F)	50
	High boiling point acetate solvent (Exxate 700)	74
	Solvent (M-Pyrol)	55.5
	Cyclohexanone	55.5

**10     Solution clear coat:**

	<u>Ingredient</u>	<u>Parts</u>
	Polymethyl methacrylate (Elvacite 2010)	50
	PVDF (Kynar 301F)	50
15	Solvent (M-Pyrol)	225
	Methethylketone	225

**Dispersion color coat:**

	<u>Ingredient</u>	<u>Parts</u>
20	DIBK (di-isobutyl ketone)	18.55
	BLO (Buytrolactone)	8.34
	Polyethyl methacrylate (Elvacite 2042)	10.20
	Cyclohexanone	9.27
25	Dispersing agent (Solsperse 17,000)	0.10
	PVDF (Kynar 301F)	24.40
	BLO	14.14
	Black dispersion	15

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1      Solution color coat:

	<u>Ingredient</u>	<u>Parts</u>
	Polyethyl methacrylate (Elvacite 2042)	10.20
5	Dispersing agent (Solsperse 17,000)	0.10
	PVDF (Kynar 301F)	24.40
	Black dispersion	15.00
	Solvent (M-Pyrol)	86.00
10	Methyethylketone	74.30

15      The dispersion clear coat was prepared by initially dissolving the Elvacite 2010 in the Exxate 700 and the cyclohexanone. The Kynar 301F was then dispersed in the resulting mixture using a high speed mixing blade from a Cowles mixer. The M-Pyrol was then added to the resulting mixture. Mixing was at room temperature so that the PVDF component remained as a dispersion in the mixture rather than dissolving. The dispersion clear coat was then coated on a casting sheet of polyester film by a reverse roll coater. The clear coat was then dried on the carrier sheet by the drying techniques described herein.

20      The solution clear coat was prepared by dissolving both resins in the solvent blend and by mixing with a high speed Cowles mixer to add sufficient heat to the mixture to completely dissolve the resin. The solution clear coat had substantially less solids (less than about 20% PVDF/ acrylic solids) than the dispersion clear coat along with use of stronger solvents to produce a clear solution PVDF/acrylic coating.

25      The dispersion color coat was prepared by dissolving the Elvacite 2042 in the DIBK and Cyclohexanone solvents along with the first part of the BLO solvent. The Kynar 301F was dispersed in the resulting mixture which was then diluted with the

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1 remaining BLO prior to adding the black dispersion. The  
black dispersion comprised carbon black dispersed in  
Elvacite 2042 and cyclohexanone.

5 The solution color coat was prepared by dissolving  
both resins in the solvent and then adding the black  
dispersion. The color coats were cast on separate  
10 polyester casting sheets, rather than coating them over  
a dried clear coat. If the base coat is cast over a  
dried clear coat, the solvents in the base coat attack  
the clear coat, especially in a solution-form base coat  
with its stronger solvents. Both color coats were then  
15 dried on their respective casting sheets.

Four thermoformable laminates were then prepared  
15 for testing gloss and DOI. Various combinations of  
dispersion clear coat, dispersion color coat, solution  
clear coat, and solution color coat PVDF/acrylic  
laminates, as described below, were prepared. Each  
20 thermoformable laminate comprised a color coat and clear  
coat laminated to an 18 mil ABS sheet. The color coat  
was first laminated to the ABS backing sheet, the  
polyester casting sheet was stripped away, then the  
25 clear coat was laminated over the color coat and the  
polyester casting sheet for the clear coat was then  
stripped away, leaving an ABS thermoformable laminate  
with the color coat and exterior clear coat bonded to a  
face of the backing sheet. The backing sheet was then  
30 subjected to deep draw thermoforming using a pressure  
assist (thermoforming temperatures were approximately  
270-280°F) to produce the test panels which were then  
measured for gloss and DOI levels.

Comparative tests of gloss and DOI for the  
dispersion and solution paint coats revealed the  
following results:

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	<u>Laminate</u>	<u>20° gloss</u>	<u>60° gloss</u>	<u>DOI</u>
1	Dispersion clear coat/ Dispersion color coat	66	82	72
5	Solution clear coat/ Dispersion color coat	69	82	82
10	Dispersion clear coat/ Solution color coat	65	81	70
15	Solution clear coat/ Solution color coat	70	81	89

These test results demonstrated that higher levels of DOI are achieved by using the solution PVDF/acrylic coatings compared with similar dispersion coatings. Moreover, the DOI levels are high, greater than about 80 units and approaching 90 units in one instance, when the laminate includes at least a clear coat of solution-form PVDF/ acrylic resin. 60° gloss levels remained about the same for solution and dispersion coatings, and these gloss levels were sufficiently high to meet exterior automotive requirements. 20° gloss levels were somewhat higher with the solution clear coat films. Best results were obtained when the paint coat comprised both a clear coat and an underlying color coat of the solution PVDF/acrylic resin.

Example 12

The chemical resistance properties of the PVDF/acrylic paint coats of this invention were compared with three other commercially used automotive paint systems. The results demonstrated that the paint coat

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1 of this invention exhibited the best chemical  
resistance. Two panels comprising PVDF/methyl  
methacrylate clear coats according to this invention  
were tested for chemical resistance (acid/alkali  
5 spotting). Three additional test panels comprised clear  
coats and pigmented base coats made from commercially  
available thermoplastic lacquer automotive paint systems  
which comprised dispersions of polymethyl methacrylate  
copolymers. Two additional tests panels comprised a  
rigid enamel, i.e., a melamine acrylic thermoset  
10 exterior automotive paint, and a flexible enamel, i.e.,  
a flexible melamine polyester thermoset exterior  
automotive paint. Several test solutions were used,  
including organic acids, G.M. acid rain, and various  
15 concentrations of sulfuric acid, hydrochloric acid and  
sodium hydroxide. The paint coats of this invention  
achieved the highest rating and were untouched by the  
different test solutions. Each of the commercial  
automotive paints experienced etching by one or more of  
20 the test solutions.

Thermoplastic Polyolefin Backing Sheet and Substrate

25 Thermoplastic polyolefins (TPO's) such as  
polypropylene and polyethylene are useful as a car body  
substrate material because of their impact resistance,  
corrosion resistance, and their ability to be formed  
into different complex configurations. Previously,  
TPO's have been difficult to paint and this has limited  
30 their use in the automotive market. Adhesion of the  
paint coat to the TPO substrate, particularly, has been  
a problem. The process of this invention can be used to  
produce an automotive quality paint coat on a TPO car  
body panel, and good adhesion can be produced between  
35 the paint coat and the TPO composite structure forming  
the underlying car body panel.

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1            Briefly, in this embodiment of the invention, a  
thin size layer of a thermoplastic chlorinated  
polyolefin (CPO) is coated between the paint coat layer  
on the flexible carrier film and the flexible TPO  
5            backing sheet. This composite structure is then  
thermoformed and bonded to a thick rigid layer of a TPO  
resin forming the substrate base for the composite car  
body panel.

10           The size coat is preferably made from a coating  
composition of a solution of the CPO. The coating  
composition contains about 10-60% by weight of the CPO  
and correspondingly about 40-90% by weight of solvent.  
Any conventional solvent can be used that will dissolve  
the CPO such as toluene or xylene. The CPO preferably  
15           is a chlorinated polypropylene or chlorinated  
polyethylene containing up to about 50% by weight  
chlorine and preferably about 15-50% by weight chlorine.  
One preferred chlorinated polypropylene is a  
20           propylene/maleic anhydride copolymer chlorinated to a  
level of about 15-50% by weight chlorine. One  
particularly preferred chlorinated polypropylene  
comprises polypropylene and maleic acid containing about  
25           18-35% by weight chlorine and having an acid no. of  
about 15.

25           The flexible backing sheet and the rigid substrate  
layer of the composite car body panel are prepared from  
standard automotive quality TPO resins, typically a  
polypropylene resin.

30           The TPO composite of this invention provides  
automotive manufacturers with many advantages over prior  
art compositions. Adhesion problems with recessed  
portions of a part are minimized, solvent emissions  
associated with spray painting, the need for expensive  
35           hangers and jigs to maintain shape of a plastic part  
during baking, and the need for a primer which is

1 required in a conventional paint spraying process all  
are eliminated. Additionally, the composite has a  
unique set of characteristics that make it superior to  
conventional injection molded and spray painted parts.

5 The color coat/clear coat of the composite of this  
invention can be cured at temperatures in excess of  
200°C versus a maximum of 125°C for conventional  
10 injection molded and spray painted plastic parts. This  
allows for the use of paint chemistries which cannot be  
used with conventional TPO parts. For example, the  
fluorocarbon polymers of this invention can be used and  
15 are substantially more durable and chemical resistant  
than conventional low bake paints.

15 The TPO used for the flexible backing sheet can be  
of a different quality than the TPO used for the rigid  
substrate layer of the composite. Presently, in the  
formation of injection molded automotive parts from TPO  
20 resins, the TPO resin must be of the highest quality,  
i.e., free of gel particles and any foreign matter, to  
ensure that a defect free part is formed with an  
automotive quality surface. Since the surface quality  
25 of the composite of this invention is determined by the  
surface of the flexible backing sheet, only the backing  
sheet need be of a high quality TPO resin, while the  
rigid substrate layer of the composite can be of a lower  
30 quality TPO resin, for example, that may contain gel  
particles and not affect the appearance of the resulting  
part or the structural integrity of the part.

The ability to separate the surface characteristic  
30 of the composite from the injection molded resin used to  
form the rigid layer of the composite allows for the  
formation of greatly improved auto parts. For example,  
fiberglass reinforced or other filler reinforced TPO's  
can be used for the injection molding resin for the

1 rigid layer of the composite, and stronger and more  
rigid parts can be formed than has been possible before.

5 The following example illustrates use of the TPO  
composite structure in a car body panel.

10 Example 13  
A thermoformed thermoplastic polyolefin (TPO)  
quarter panel for a Pontiac Fiero having an exterior  
high gloss jet black automotive paint was formed. The  
paint coat was first coated onto a surface of a sheet of  
flexible polyester film. The film is a 50 micron thick  
high gloss duPont Mylar 200A polyester film. The paint  
layers coated onto the film were a clear coat, a color  
coat and a chlorinated polyolefin size coat. Each was  
15 coated onto the polyester film in that order.

A clear coating composition was prepared as  
follows:

	<u>Ingredient</u>	<u>Parts</u>
20	Methylethyl ketone	40.85
	Butyrolactone	40.85
15	Elvacite 2021 - (Polymethyl methacrylate having a weight average Mw of 200,000)	6.22
25	UV absorber [Tinuvin 900-2-hydroxy- 3,5-di[1,1-dimethyl(benzyl)phenyl]- 2H-benzotriazole]	0.35
	Hindered amine light stabilizer- [Tinuvin 292-bis(1,2,2,6,6-penta- methyl-4 piperidinyl)sebacate]	0.18
30	Kynar 301F	11.15

35 The solid ingredients were added to the methyl  
ethyl ketone and butyrolactone solvents with mixing and  
mixing was continued until dissolved. The film forming  
binder of the coating contained about 65% PVDF and 35%

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1 polymethyl methacrylate. The clear coating was applied  
by reverse roll coater to the polyester film. The clear  
coat was dried on the polyester film by passing it  
through a multi-zone impinging air drying oven having  
5 three heating zones spaced apart axially along the  
length of the carrier, with each drying zone having a  
progressively higher temperature. The clear-coated  
polyester sheet was passed through the heating zones at  
a line speed of about 7.5 meters per minute; each  
10 heating zone was about 12 meters long. Temperatures of  
the three heating zones were: Zone 1: 125°C; Zone 2:  
165°C; Zone 4: 200°C. By passing the clear coated  
polyester sheet through the three heating zones,  
substantially all solvent gases from the clear coat were  
15 removed to produce a dry clear coat of uniform film  
thickness about 20 microns thick.

A jet black color coating composition was  
formulated as follows:

	<u>Ingredient</u>	<u>Parts</u>
20	Cyclohexanone	9.27
	Diisobutyl ketone	18.54
	Butyrolactone	8.34
	Elvacite 2042 =(polyethyl methacrylate having a weight average Mw 300,000)	10.02
25	Solsperse 17,000 Dispersing agent	0.10
	Kynar 301F	24.04
	Butyrolactone	14.14
	Black Pigment Dispersion	15.00

30 The black pigment dispersion comprised carbon black  
in a vehicle of Elvacite 2043 (polyethyl methacrylate)  
available commercially as Gibraltar 438-39110 pigment.

35 The color coating composition was prepared by first  
dissolving the acrylic resin in the cyclohexanone,  
diisobutyl ketone and butyrolactone solvents at a

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1       temperature of about 55°C and then allowing it to cool  
before the polyvinyl fluoride component was added to the  
mixture to form a dispersion of the PVDF in the acrylic  
resin. The black pigment dispersion was then added to  
5       the resulting mixture to produce the jet black color  
coating composition. On a weight basis, the amount of  
pigment contained in the color coating was about 4-5%.  
The binder of the coating contained about 65% PVDF and  
10      35% acrylic resin by weight. The acrylic resin  
component comprised about 90% Elvacite 2042 and 10%  
Elvacite 2043. The color coating composition was coated  
onto the dried clear coat as above and then passed  
through the three stage oven described above to dry the  
color coating and form a dry color coating layer about  
15      20 microns thick.

A CPO (chlorinated polyolefin) size coating  
composition for use with a TPO backing sheet was  
formulated as follows:

	<u>Ingredient</u>	<u>Parts</u>
20	Xylene	24.60
	Chlorinated polyolefin (CPO) solution (Eastman's CP-343-1 25% solids in xylene of chlorinated polypropylene/maleic acid polymer, acid no. about 15, chlorine content about 18-23%)	25.00
25	Toluene	42.50
	N-methyl pyrrolidone	1.00
	Acrylic Dispersion Resin (60% solids of an acrylic vinyl oxazoline ester polymer described in Example 1 of Miller U.S. Patent 3,844,993)	6.90

The binder of the size coating composition  
35      contained about 60% CPO and about 40% acrylic resin by

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1 weight. The size coat composition was coated onto the  
dried color coat to a dry film thickness of about 2.5  
microns using the reverse roll coater. The three  
temperature zones were maintained at the same  
5 temperature as used for the clear and color coats but a  
carrier speed 30 meters per minute was used.

10 The resulting paint coated polyester film was then  
passed to a laminating operation illustrated in FIG. 2,  
where the paint coat of the polyester film was  
transferred to a 500 micron thick TPO backing sheet made  
from RPI E-1000, thermoplastic olefinic elastomer from  
15 Republic Plastics Company, to form a face sheet. RPI E-  
1000 has a flexural modulus of approximately 690 MPa and  
a melt flow rate of approximately 0.8 g/10 min. In the  
laminating operation, the backing sheet and the paint  
coated polyester film carrier were run at a lineal speed  
20 of 5 meters per minute, and the laminating drum was  
operated at a temperature of 177°C. The CPO size coat  
was heat activated and the paint coat was transferred  
from the polyester film to the face of the TPO backing  
sheet during the laminating operation, in which the hot  
steel drum applied a force of about 54 kg/lineal cm to  
form the face sheet. The polyester film was stripped  
25 away from the surface of the face sheet, leaving the  
paint coat bonded to the TPO sheet, with the clear coat  
providing a high gloss surface on the exterior of the  
TPO backing sheet.

30 The resulting face sheet was then thermoformed into  
a complex three-dimension shape to form a plastic  
quarter panel molding. In the thermoforming process,  
the face sheet was first heated to a temperature of  
about 121°C to soften the face sheet. The heated face  
sheet then was placed over a pressure assist vacuum  
former buck and a vacuum was drawn against the buck on  
35 the TPO side of the face sheet and 2.1 kg/cm<sup>2</sup> gauge of

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1 air pressure applied on the clear coat side of the  
laminate to form the heated face sheet into the three  
dimensional shape of the quarter panel.

5 The resulting thermoformed laminate was then  
trimmed to fit in the mold cavity of a plastic injection  
molding machine. A quarter panel was then formed. An  
elastomeric thermoplastic alloy molding resin RTA-3263  
from Republic Plastics Company, having a flexural  
modulus of about 1725 MPa was used for forming the base  
10 of the quarter panel. The resin was injected into the  
mold behind the thermoformed laminate, fusing the resin  
to the TPO base of the laminate to form the quarter  
panel about 2.5-3.75 mm thick. The mold was operated at  
the normal melt temperature for the resin. A quarter  
15 panel was formed that is an integral plastic  
composite part with a defect-free paint coat on the  
exterior surface of the panel.

20 The quarter panel was tested and the tests  
demonstrated the usefulness of the paint coat as an  
exterior automotive finish. The test results indicated  
that desirable appearance properties, including gloss,  
were produced. Specular reflectance measured units 70  
units at 20°. gloss and DOI measured 85 units. Color  
uniformity was good. The test results also demonstrated  
25 a desirable combination of durability properties. The  
test panel passed tests for gasoline resistance, acid  
resistance, chip resistance (gravelometer reading of 9),  
impact resistance (80 in./lb. for Gardner Test), and  
passed QUV and 96 hour humidity exposure tests.

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Water Soluble Protective Coatings

As disclosed previously, a thin film of wax can be  
coated onto the flexible carrier sheet prior to casting  
the clear coat onto the carrier. The wax film can serve

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1       as a protective layer for the finished painted car body  
panel.

5       In addition, a separate water soluble protective  
coating can be applied to the clear coat (or to the wax  
10      film on the clear coat) during processing so that the  
water soluble layer is available to provide a protective  
mar resistant exterior coating for the finished car body  
panel, through assembly of the automobile and shipment  
15      to the purchaser. The coating is preferably a low  
molecular weight material which adheres to the clear  
coat throughout processing and can be buffed to a glossy  
finish.

20      Preferably, the water soluble protective coating is  
overstamped as a barrier film onto the dried clear coat.  
25      The clear coat and color coat are cast on a polyester  
carrier film and bonded to the flexible backing sheet as  
described previously. Separately, a water soluble  
coating such as polyvinyl alcohol (PVA) is coated onto a  
flexible polyester carrier sheet and dried. After the  
carrier film is stripped away from the surface of the  
clear coat, the PVA film is overstamped onto the surface  
of the clear coat, preferably by pressure roll  
techniques. The PVA is separately cast so that it is  
not subjected to solvent attack from the clear coat and  
so that it would not interfere with the transfer of  
gloss to the surface of the clear coat from the  
polyester casting film. The polyester carrier film is  
then stripped away from the PVA layer, leaving a water  
soluble protective film of PVA bonded to the exterior  
30      surface of the clear coat. The resulting backing sheet  
is then subjected to further processing, including  
thermoforming and injection-cladding, leaving a finished  
car body panel with the water soluble protective outer  
coating. This coating can then be easily buffed or  
35      removed with water by the auto dealer or purchaser.

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Controlled Flop/Head-on Brightness

The color coats used in this process can include metallic flake pigments. When a metallic flake pigment dries on a substrate surface, the flakes generally become oriented in parallel to the surface of the substrate. These orientations can vary, however, especially with spray painting, which can cause substantial disorientation and resulting differences in the apparent color of the finished paint. Visual color comparisons of metallic paints can be made by known procedures for measuring such parameters as flop index and head-on brightness (HOB). (These measurements are described in U.S. Patent No. 4,692,481 to Kelly, which is incorporated herein by this reference.) A finished paint coat with well-oriented metallic flakes has desirable high flop and HOB values. The process of this invention can be used to produce a finished metallic flake paint coat with high flop and HOB values. The metallic flake color coat can be coated separately onto its polyester carrier film and slowly dried on the film to carefully align the metallic flakes in a parallel orientation, achieving high flop and HOB values. The pre-aligned metallic flake pigment is then subjected to further processing (transfer to the backing sheet, thermoforming, and injection-cladding, for example) to produce a finished car body panel with the high flop and HOB values. The linear orientation of the flakes is not disrupted during further processing and is thought to be enhanced by the elongation occurring during thermoforming. The high values for flop and HOB are substantially higher than with spray painting a similar substrate.

In addition, even higher HOB values are produced when the paint coat of this invention uses metallic

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1 flakes with a thickness of less than about 2000  
Angstroms. An example of these flakes is available from  
Avery Decorative Film Division of Avery International.  
These metallic flakes are sold as L-53520 and identified  
5 as Bright Aluminum Flake. The paint coat of this  
invention, when using these metallic flakes, can achieve  
an HOB value of greater than 140 units, for a pure  
silver color coat.

10 Pigmented Backing Sheet

Improvements can be provided by using a pigmented  
backing sheet in the process of this invention.  
Experiments have shown that light transmission through a  
paint-coated laminate is reduced when a pigmented  
15 backing sheet is used in the process, as compared with a  
clear backing sheet. These experiments included  
measuring light transmission through a white paint coat  
laminated to a black backing sheet (the paint coat  
comprised a clear coat and underlying white color coat),  
20 compared with measuring light transmission through the  
same white paint coat laminated to a clear backing  
sheet. The pigmented backing sheet increases opacity  
substantially, thereby reducing the amount of pigment  
required in the color coat to hide defects in the  
25 underlying substrate.

Pre-Applied Graphics

Printed graphics can be incorporated into the  
process of this invention. In one process for applying  
30 graphics to the finished paint coat, the clear coat is  
first cast onto the flexible polyester carrier film.  
The clear coat is then dried on its carrier film. The  
graphics pattern is then printed on the surface of the  
dried clear coat opposite from the carrier film. The  
35 graphics pattern can be any desired pinstriping pattern,

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for example. The color coat also is cast on the clear coat and over the graphics pattern and dried. This leaves the clear coat on its carrier film with the pre-applied graphics and color coat visible through the clear coat. Alternatively, the color coat can be cast in a separate carrier film and then transferred in dry film form over the pre-printed graphics pattern and onto the dried clear coat. A suitable size coat is then applied to the surface of the dried color coat, and the resulting laminate is transferred to the flexible backing sheet by the techniques described previously. The carrier film is stripped away in this process, and the resulting paint-coated laminate is thermoformed into the desired shape to form a mold insert. The resulting mold insert is then injection clad with the desired substrate material to form the finished car body panel. An advantage of this process is that graphics patterns are printed under an automotive quality clear coat, which provides a smooth exterior surface on the finished car body panel protecting the underlying graphics. The graphics are therefore not subject to wax or dirt build-up around them as is the case presently with graphics applied to the surface of a finished exterior paint coat.

Thus, the present invention provides a dry paint process and paint system which produce a useful blend of durability, chemical and visual appearance properties. The paint coat has a combination of durability, gloss, resistance to deglossing, and elongation that produce and retain exterior automotive properties in the paint coat throughout the processing steps. As one advantage, the invention makes it possible to use high molecular weight PVDF in an OEM exterior paint for plastic car bodies, despite the temperature limitations of molded

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1 plastic materials and the fact that PVDF normally  
requires use of strong solvents and high temperatures to  
form glossy films from this polymer. By alloying PVDF  
5 polymers with acrylic polymers, the result is a paint  
coat with superior mechanical properties, including  
exterior durability, chemical resistance and toughness.  
The low surface energy surfaces characteristic of  
10 fluoropolymers also provide enhanced washability and  
produce a high contact angle "beading" surface requiring  
little or no waxing. As a further advantage, the dry  
paint process allows part production and coating to be  
coincidental with the other manufacturing operations at  
an automobile production plant by transferring quality  
15 control, solvent emission problems and color control to  
an outside supplier. This can eliminate from the auto  
plant the conventional coating operations, including  
application lines and ovens.

As a further advantage, the dry paint process can  
be extended to producing a flexible self-adhesive  
20 laminate for use in automotive refinishing. Fig. 14  
illustrates one embodiment of such a laminate 140 which  
can allow rapid refinishing of an exterior automotive  
paint coat with greatly reduced surface preparation  
requirements. The flexible laminate comprises a  
25 removable masking 141, the clear coat 45 bonded to the  
color coat 46 (although a single paint coat having  
exterior automotive properties can be used as an  
alternative to the separate clear coat and color coat),  
a flexible backing 142 adhered to the color coat 46, a  
30 pressure-sensitive adhesive 144 on the flexible backing,  
and a release backing 146 covering the pressure-  
sensitive adhesive. This laminate can be tolerant to  
rough surfaces and develop good adhesion because of the  
35 conformability provided by its flexibility and the  
pressure-sensitive adhesive backing. By applying a

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1        trimmable self-adhesive sheet for large and small areas,  
it can have application to skilled refinishers as well  
as use for the consumer market by eliminating the need  
for large paint booths and ovens, capital investment,  
5        and environmental emission problems normally associated  
with exterior automotive refinishing.

Although the invention has been described as  
relating to automotive quality paint coats applied to  
car body panels, it is to be understood that the  
invention is not limited solely to automotive uses or  
exterior automotive panels. The invention is also  
applicable to other vehicles requiring automotive-  
quality exterior paint coats. Trucks, motorcycles,  
boats, dune buggies, and the like are examples.  
15      Moreover, the invention is applicable to a variety of  
exterior body members or parts of motor vehicles.  
Bumpers, fender extensions, wheel covers, hub caps, trim  
rings for wheels, lamp housings, grills and other  
exterior facia components or parts are examples of other  
20      substrates to which the paint coat can be applied, in  
addition to conventional exterior body parts or panels  
of the vehicle.

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